Polymer Bulletin 19, 493–500 (1988)

Polymer Bulletin

Physical chemistry of polyelectrolytes

1. Viscometry of a polyacid in salt-free aqueous solution

László Korecz, Éva Csákvári, and Ferenc Tüdos*

Central Research Institute for Chemistry of the Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

SUMMARY

The viscometric behavior of poly(1-vinyl-2-pyrrolidone-co-maleic acid) samples of different molecular mass values (determined by absolute methods [1,2]) was studied in dilute salt-free aqueous solutions. An $f(c)=(a_0+a_1c)c^k$ type empirical equation was found appropriate to describe the concentration dependence of the specific viscosity. The advantage of the proposed formula over other suggested empirical equations arises from the fact that it involves the relationship valid for uncharged polymers in a limitation case.

INTRODUCTION

In spite of the attention to polyelectrolytes renewed periodically on account of the extensively developed application area, the knowledge concerning the fundamental points of the physical chemistry of charged macromolecules has still remained insufficient. Special interest has been devoted to properties and behaviour of water-soluble synthetic polymers [3,4].

The determination of direct characteristics encounters considerable difficulties in most cases, therefore, the studies of polyelectrolytes has taken a direction aiming the determination of indirect, system-specific features, such as the intrinsic viscosity in certain solvents, mainly in salt solutions. Unfortunately, inconsistency in the interpretation of direct and indirect parameters occurs quite frequently, although, obvious distinction would be desirable for practical and theoretical reasons equally.

The scope of our new serial is planned to serve as a direct contribution to the physical chemistry of polyelectrolytes by continuing the systematic studies on a hydrolytically stable water-soluble polyacid, poly/1-vinyl-2-pyrrolidone-co-maleic acid/, published hitherto with a serial title: "Physico-chemical Studies of Polymeric Carriers".

The aim of the present work is to study the viscometric behaviour of P/NVP-co-MAc/ samples of different molecular mass values. The direct characteristics of the samples ($\overline{M}_w$ values) were determined by absolute methods (light scattering and sedimentation-diffusion equilibrium measurements) applying the conception of suppressing the dissociation of the polyacid [1,2,5].

In the case of charged macromolecules, the characterization by the indirect, system-specific intrinsic viscosity [η] as accepted for uncharged linear homopolymers, has been hindered by

---

* To whom offprint requests should be sent

the characteristic profile of the reduced specific viscosity η_{sp}/c vs. polymer concentration c function of aqueous polyelectrolyte solutions. Although, in those cases, where the determination of direct parameters involves difficulties (see e.g. in Introduction in ref. [2]), a less valuable, but more or less informative parameter might be acceptable. Attempts have generally been made to solve this problem in two different manner: 1.) by screening of charges via added salt, 2.) by empirical equations. It should be noted, that although the η_{sp}/c vs. c function can be generally linearized by screening of charges by salts added in 1-2 M concentrations, the dissociation of polyanions or polycations can not be suppressed in this way [6,7]. Furthermore, from thermodynamic point of view, a more complex situation can be generated in such cases [8]. Thus, the 2nd mode lookds more promising to evaluate indirect parameters.

The widely applied empirical equation of Fuoss was set up originally for aqueous solutions of strong polyelectrolytes [9], and as the author stressed later, was in no case intended by him for application to mixtures of polyelectrolytes with simple electrolytes [10]. The original form of the Fuoss equation is the following:

$$\frac{\eta_{sp}}{c} = \frac{A}{[1 + Bc^{1/2}]} + D \qquad (1)$$

where A, B, D are constants and $\lim_{c \to 0} \eta_{sp}/c = A + D$, i.e., the sum of A and D is an analogue quantity of the intrinsic viscosity $[\eta]$. If $D \ll A$, then the function of c/η_{sp} vs. $c^{1/2}$ is linear.

The above equation can be successfully applied to describe the behaviour of polyelectrolytes widely, but it has not involved in a limitation case the relationship valid for uncharged polymers. We intended to set up an empirical relationship fulfilling both criterions.

EXPERIMENTAL

Four sets of viscosity measurements were made in an Ubbelohde viscometer at 25 ± 0,1 °C applying different P/NVP-co-MAc/ samples: $\bar{M}_w = 11\ 000$, $20\ 000$, $31\ 000$ and $44\ 600$. The hydrolysis of the crude poly/1-vinyl-2-pyrrolidone-co-maleic anhydride/ polymers and the purification of the polyacid samples were carried out as described in ref.[5]. The primary characteristics, i.e., $\bar{M}_w$ values were determined by viscometry using the Mark-Houwink equation for the very case, based on light scattering and viscometry of P/NVP-co-MAc/ fractions [1,5] and by ultracentrifugation [2], both in 0.0085 M HCl solutions, where the dissociation of thepolyacid could be suppressed, consequently, the absolute methods have become applicable.

Double distilled water was applied for the preparation of the stock solutions and for further dilution. Prior to measurements, all the solutions and the solvent were subjected to filtration (on G4 sintered glass filter) adopting the careful handling practice essential in light scattering, applied also in conscientious viscometric studies in order to avoid any possible disturbing effects due to solid contamination.

RESULTS AND DISCUSSION

The usual profile of η_{sp}/c versus c function typifying polyelectrolytes was obtained in all cases for the P/NVP-co-MAc/ samples of different $\bar{M}_w$ values as illustrated in Fig.1.

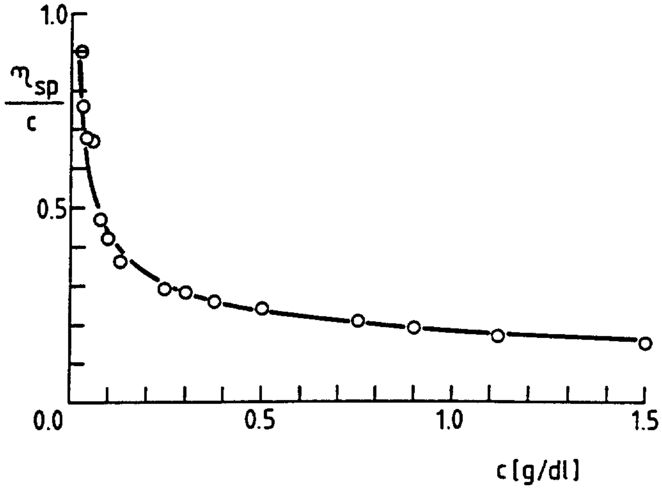

Fig.1. A plot of reduced viscosity vs. concentration of P/NVP-co-MAc/ in dilute aqueous solution at 25 °C, $\bar{M}_w$ = 11 000.

Since the limiting value of $\lim_{c\to 0} \eta_{sp}/c$ is not an a priori existing value, we have found more promising to analyse the concentration function of the specific viscosity, $\eta_{sp} = f(c)$. This kind of treatment has got the advantage that $\lim_{c\to 0} \eta_{sp} = 0$ is an obviously specified criterion fulfilled in all cases so that the choice of the proper function fitting the experimental points best, can be facilitated.

Good correlation can be attained by fitting with $f(c) = a\cdot c^k$ type functions in all studied cases. The values obtained for a, k are listed in Tab.1, where the squares of the correlation coefficients (R^2) are also given. The fitting was performed by applying the least-squares method. An illustrating fitting is shown in Fig.2 in double logarithmic plotting. The values of the corresponding correlation coefficient are practically 1, consequently, the power function can be successfully applied for fitting the experimental results.

Tab.1 Fitting parameters for the concentration dependence of the specific viscosity and relationships between the non-electrolytic characteristics ($\underline{a}$ or $\underline{a}_0$) and the molecular mass ($\overline{M}_w$) in the case of poly/1-vinyl-2-pyrrolidone-co-maleic acid/ in dilute, salt-free aqueous solutions at 25 °C.

M_w	$\eta_{sp} = a \cdot c^k$			$\eta_{sp} = (a_0 + a_1 c)c^k$		
	R^2	a	k	R^2	a_0	a_1
11 000	0.9761	0.172	0.572	0.6765	0.158	$2.334 \cdot 10^{-2}$
20 000	0.9881	0.269	0.656	0.9393	0.235	$5.022 \cdot 10^{-2}$
30 800	0.9917	0.368	0.528	0.9426	0.332	$4.513 \cdot 10^{-2}$
44 600	0.9944	0.418	0.427	0.9746	0.385	$7.004 \cdot 10^{-2}$
	$a = 4.14 \cdot 10^{-4} \cdot M^{0.65}$ $R^2 = 0.9826$			$a_0 = 3.60 \cdot 10^{-4} \cdot M^{0.66}$ $R^2 = 0.9899$		

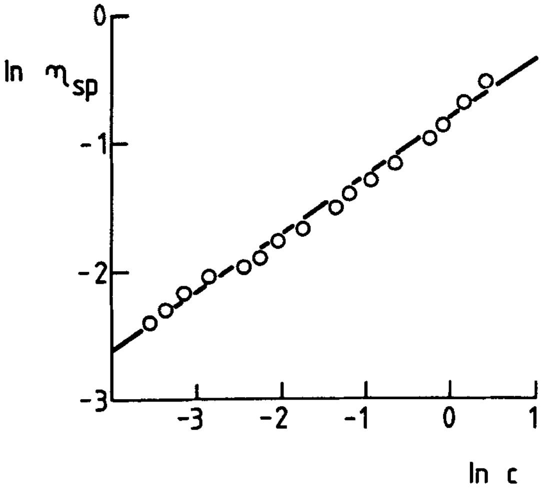

Fig.2. An illustration for the fitting of the concentration dependence of the specific viscosity with $f(c) = a \cdot c^k$ type function for P/NVP-co-MAc/ in dilute aqueous solution at 25 °C, $\overline{M}_w = 44\ 600$.

It was found also necessary to examine whether the scattering points were randomly or systematically distributed. This can be checked by analysing the concentration dependence of η_{sp}/c^k. The transformation of $\eta_{sp} = f(c)$ function has led to the conclusion that the scattering is systematic and can be described by the following function: $\eta_{sp}/c^k = a_0 + a_1 c$ within the usual concentration range. At concentrations $\underline{c} < 0.1$ g/dl, as it has often been reported for such systems, the experimental points show considerable spreading. The η_{sp}/c^k vs. $\underline{c}$ functions are shown in Fig.3. An additional curve is also given in Fig.3, derived from the data of Rios et al. [11] determined for a P/NVP-co-MAc/ sample in water at 25 °C. Although, the number of the points in the latter case is unfortunately rather few (only 5), and besides, the concentration range covered is narrow, our fitting with the power function gives fairly good results: $a = 0.15$, $k = 0.61$, $R^2 = 0.99$ (cf. Fig.3 and Tab.1).

The actual values of a_0 and a_1 together with the corresponding R^2 values are listed in Tab.1.

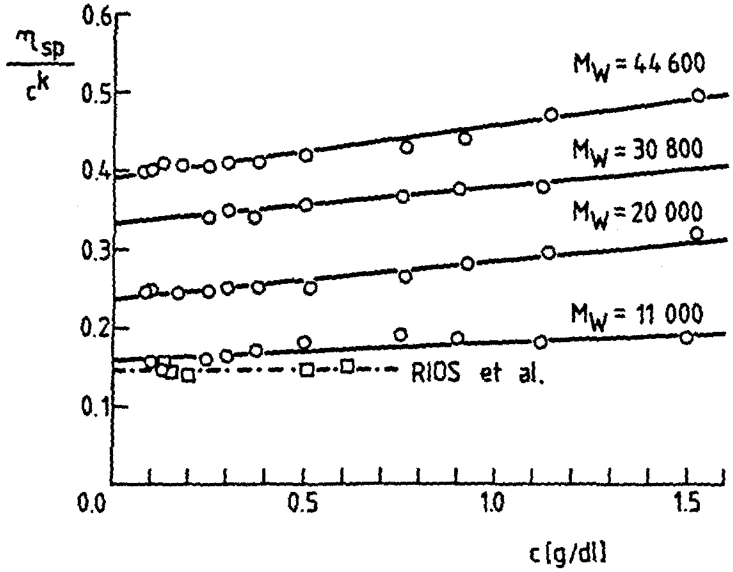

Fig.3. Illustration of the separation of electrolytic and non-electrolytic viscometric characteristics of P/NVP-co-MAc/ samples with $\eta_{sp}/c^k = a_0 + a_1c$ *type functions, in dilute aqueous solution at 25 °C; a function derived from data of Rios et al. [11] is also given (□).*

According to the above considerations, we suggest an

$$f(c) = (a_0 + a_1c)c^k \qquad (2)$$

type empirical equation for the description of the concentration dependence of the specific viscosity of dilute, salt-free aqueous polyacid solutions. In order to clear up the physical meaning of the constants in our empirical relationship, let the function be transformed into a form similar to that accepted for uncharged polymers:

$$\frac{\eta_{sp}}{c} = (a_0 + a_1c)c^{k-1} \qquad (3)$$

If k = 1, the function valid for uncharged macromolecules is regained. Thus, a_0 being an analogue quantity of the intrinsic viscosity can be considered together with a_1 as viscometric characteristics of a hypothetically uncharged polymer. Presumedly, the fractional power function of the concentration involves the electrolytic character of the polyacid. The simple power function of the concentration can be considered as an approximation of a more complex function since the effect of charges on the actual value of the viscosity is probably a consequence of different, combined factors.

Actually, such a formal separation of the electrolytic and non-electrolytic contributions of a dilute, salt-free aqueous polyelectrolyte to its viscometric behaviour, makes possible to set up an equation between the data pairs $\underline{a}_0$ (or its approximate value: $\underline{a}$) accepted as the intrinsic viscosity of a hypothetically uncharged polymer and $\underline{M}_w$ determined independently. $\underline{\alpha}$, $\underline{K}$ constants for P/NVP-co-MAc/ valid in dilute, salt-free aqueous solutions at 25 °C are presented in Tab.1.

For practical reasons it would be desirable to distinguish parameters independent of M_w as well beside the separation of electrolytic and non-electrolytic characteristics of the polyacid. Such a kind of cut-and-try methods might serve as a convenient, fast way for the estimation of the molecular mass. Unambigous distinction can not be made on the basis of the data available (see k, a_1 values in Tab.1). Presuming that a_0 and a_1 can be expressed as functions of parameters independent of M_w and ones depending on it:

$$a_0 = \beta_0 \cdot M^{-0.65} \tag{4}$$

$$a_1 = \beta_1 \cdot M^{-0.65} \tag{5}$$

η_{sp} can be expressed in the following form:

$$\eta_{sp} = M^{0.65}(\beta_0 + \beta_1 c)c^k \tag{6}$$

Replacing β_0, β_1 and k in eq.6 by their mean values, expression for M_w is obtained:

$$M_w = \left(\frac{\eta_{sp}}{(\beta_0 + \beta_1 c)\, c^k}\right)^{1/0.65} \tag{7}$$

Testing of eq.6 is given in Fig.4., where it is clearly shown, that the molecular mass values of the studied samples can be obtained with acceptable accuracy (±5 %) in the vicinity of $c = 0.9$ g/dl.

It should be noted, that although both β_1 and k show considerable scattering (see Tab.2), the above expression for M works as a "single-point-method". No theory is available at present to predict such a phenomenon.

Tab.2 Numerical values and standard deviations of the parameters: $\bar{\beta}_0$, $\bar{\beta}_1$, $\bar{k}$

Numerical values	Standard deviations
$\bar{\beta}_0 = 37.954 \cdot 10^{-5}$	$1.537 \cdot 10^{-5}$
$\bar{\beta}_1 = 6.422 \cdot 10^{-5}$	$1.210 \cdot 10^{-5}$
$\bar{k} = 0.54575$	0.09533

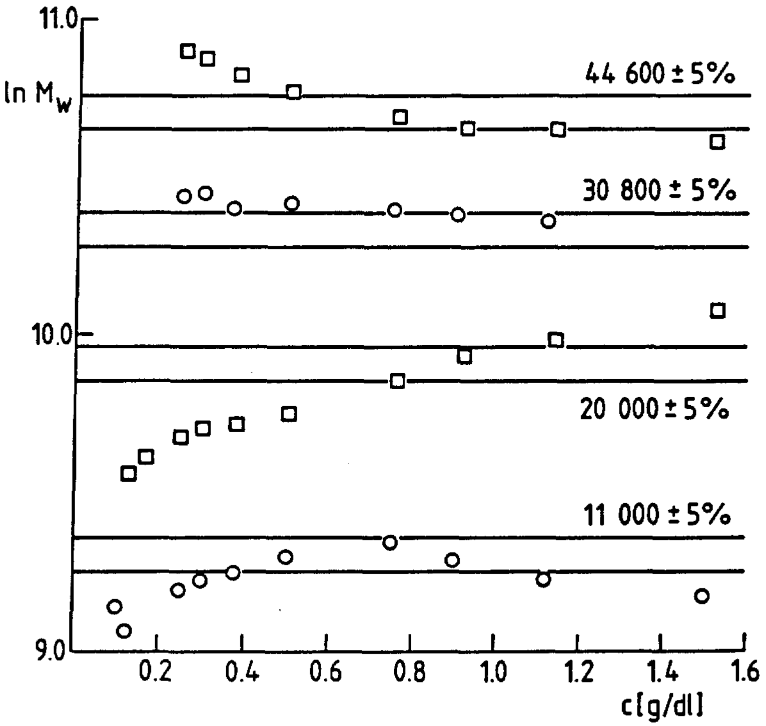

Fig.4. The concentration dependence of M_w estimated by applying eq.6.

ACKNOWLEDGEMENT

The work was supported by the National Scientific Research Foundation.

The authors are thankful to Dr.Mária Azori for the kindly supplied poly/1-vinyl-2-pyrrolidone-co-maleic anhydride/ samples. The authors thank Mrs. E. Suppán for technical assistance.

REFERENCES

1. É.Csákvári, M.Azori, F.Tüdős, Polym.Bull. 5, 673 (1981).
2. É.Csákvári, L.Korecz, M.Azori, F.Tüdős, Polym.Bull. 17, 557, (1987).
3. P.Molyneux, "Water-Soluble Synthetic Polymers: Properties and Behaviour" ed. by Macrophile Associates, CRC Press, Boca Raton, Florida (1983/1984).
4. P.Molyneux, "Water-Soluble Synthetic Polymers, Update I" ed. by Macrophile Associates, compiled and edited by P.Molyneux, CRC Press, Boca Raton, Florida (1987).
5. É.Csákvári, M.Azori, F.Tüdős, Polym.Bull. 5, 413 (1981).
6. H.Fujita, T.Homma, J.Polym.Sci. 15, 277 (1955).
7. I.Kagawa, R.M.Fuoss, J.Polym.Sci. 18, 535 (1955).
8. H.Fujita, "Mathematical Theory of Sedimentation Analysis"

in a Series of Monographs "Physical Chemistry", ed. by E.Hutchinson, P.van Rysselberghe, Academic Press, New York (1962).
9. R.M.Fuoss, J.Polym.Sci. 3, 603 (1948).
10. R.M.Fuoss, J.Polym.Sci. 12, 185 (1954).
11. H.Rios, L.Gargallo, D.Radic, J.Polym.Sci., Polym.Phys. 24, 2421 (1986).

Accepted February 3, 1988 C