

ELECTROPHORETIC BEHAVIOUR OF UNDISSOCIABLE POLYMERS IN AQUEOUS SALT SOLUTIONS

E. PROKOPOVÁ and M. BOHDANECKÝ

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

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Solutions of poly(2-hydroxyethyl methacrylate) were studied in aqueous solutions of magnesium perchlorate at high ionic strength values by the method of free electrophoresis, at different degrees of polymerization and concentrations of the polymer. The electrophoretic mobilities thus determined were used for approximate calculations of the charge.

Investigations of the properties of poly(2-hydroxyethyl methacrylate) revealed that this polymer, which is insoluble in water, can be dissolved in aqueous solutions of some neutral salts (perchlorates, thiocyanates) if the concentration of the salt exceeds a certain characteristic limit¹. Although it is known that the solubility of hydrophilic undissociable polymers can be affected, both favourably and unfavourably, by neutral salts, the causes of this phenomenon remain still unexplained. This is why we regarded it as useful to investigate electrophoretically the solutions of poly(2-hydroxyethyl methacrylate) in aqueous salt solutions. It has been our objective to find out whether there exists an interaction between the polymer and the ions which would change the undissociable molecules, immobile in the electric field, into particles which are electrophoretically active.

EXPERIMENTAL

Four fractions of poly(2-hydroxyethyl methacrylate) obtained by precipitation fractionation of the products of radical polymerization were used in the experiments. The molecular weights M (Table I) were calculated from intrinsic viscosity in dimethylformamide¹.

The apparatus for free electrophoresis made in Czechoslovakia and the experimental technique have been described earlier². The solutions of poly(2-hydroxyethyl methacrylate) in 0.2M, and exceptionally also in 0.3M- $\text{Mg}(\text{ClO}_4)_2$ solution, *i.e.* at the ionic strength 0.6 and 0.9 respectively, were measured at 4°C without any preceding dialysis. The polymer was still well soluble under these conditions at the maximum solution concentration $c_p=0.2\%$. The specific conductivity of the polymer solutions in all experiments was the same as the conductivity of solutions of pure salt, *i.e.* $\kappa = 1.55 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$ in 0.2M salt solution and $\kappa = 2.14 \cdot 10^{-2} \Omega^{-1} \text{cm}^{-1}$ in 0.3M salt solution. The measurements were performed at a potential gradient of 2.6 V/cm. The mobility (u) was calculated from the velocity of movement of the maximum of the gradient curves. Its dimension is given in the results as $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$.

TABLE I

Dependence of Limiting Mobility (u in $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) on Molecular Weight of Poly(2-Hydroxyethyl Methacrylate) in 0.2M- $\text{Mg}(\text{ClO}_4)_2$ at $c_p = 0.1$ g/dl

Fraction	I	II	III	IV
$M \cdot 10^{-3}$	17	80	275	427
$u_d \cdot 10^5$	1.97	2.04	2.06	2.07 (1.10 ^a)
$u_a \cdot 10^5$	2.27	2.48	2.17	2.10 (1.40 ^a)

^a Mobility in 0.3M solution of $\text{Mg}(\text{ClO}_4)_2$ at $c_p = 0.05$ g/dl.

The highest fraction was measured in solutions having the ionic strength $I = 0.6$ at different polymer concentrations (c_p) and in a solution having the ionic strength $I = 0.9$ at the concentration $c_p = 0.05\%$. The dependence on molecular weight was investigated at $c_p = 0.1\%$ and $I = 0.6$.

RESULTS AND DISCUSSION

Magnesium perchlorate was chosen as the most suitable of a number of salts in the aqueous solutions of which poly(2-hydroxyethyl methacrylate) is soluble¹, since the limiting concentration needed for the polymer to be dissolved in it is only 0.2M, while for sodium perchlorate and thiocyanates these concentrations are several times higher, and therefore not suited for electrophoretic measurements. It should be said, however, that even concentrations ranging from 0.2 to 0.3M of magnesium perchlorate were rather high for electrophoretic measurements, so that no further increase in the concentration was possible.

Under the given conditions, the polymer molecules migrate in the electric field as anions. It can be deduced therefrom that it is the perchlorate anion that is preferentially bonded onto them. Both boundaries are relatively symmetrical and enantiographic.

The dependence of the mobility on the polymer concentration, c_p , seems rather remarkable (repeated experiments showed that there was no artefact involved here). The curve (Fig. 1) starts from the very beginning or from a point on the y -axis very close to the beginning and quickly reaches the limit at $c_p \sim 0.05$ g/dl. The difference between the mobilities of the descending (u_d) and the ascending boundary (u_a) observed at the lowest polymer concentration practically disappears at a concentration higher than 0.1 g/dl, *i.e.* at the limiting mobility values.

The mobility of the polymer decreases with increasing salt concentration (Table I). With respect to the very narrow range of the salt concentration which it was possible to use for the measurements the effect of the salt concentration on mobility cannot be discussed in detail.

The limiting mobility is practically independent of the molecular weight of the polymer and approximately eight times lower than the mobility of totally dissociated molecules of synthetic polyelectrolytes measured at the same temperature and at the ionic strength 0.1 (polyacrylic, polymethacrylic, and polyvinylsulphonic acid²). According to Hermans and Fujita³, the independence of the mobility on the molecular

weight means that the complex poly(2-hydroxyethyl methacrylate)-perchlorate anion behaves in the electric field as a free-draining coil whose mobility is equal to the mobility of the segment:

$$u = Q_s/f_s = Q_{\text{fix}}/Nf_s, \quad (1)$$

where Q_s is the fixed charge of the segment, N is the number of segments in the macromolecule, Q_{fix} is the fixed charge of the macromolecule proportional to the molecular weight of the polymer, and f_s is the frictional resistance of the segment. Here we meet with an uncertainty concerning the question which part of the macromolecule should be regarded as a segment. The most appropriate definition of the "electrophoretic segment" seems to be that of Noda and coworkers⁴, who defined it as a sequence of monomer units carrying one unit charge. It then holds for the mobility (in electrostatic units)

$$u = 4.8 \cdot 10^{-10}/300f_{\text{es}}, \quad (2)$$

which allows a calculation of the frictional coefficient of the electrophoretic segment f_{es} . Our measurements in 0.2M perchlorate solution give $f_{\text{es}} = 8 \cdot 10^{-8}$ for $c_p \geq 0.05$ g/dl and $f_{\text{es}} = 16 \cdot 10^{-8}$ for $c_p = 0.025$ g/dl.

An attempt will now be made to estimate the order of magnitude of the segment and charge of the macromolecule of poly(2-hydroxyethyl methacrylate). The first estimate is based on an empirical correlation⁵ between the mobility of the anions of monobasic acids and their size expressed in terms of the total number of atoms, n . A mobility of $25 \cdot 10^{-5}$ corresponds to the highest available value $n = 40$. Owing to the extent of the correlated data, an extrapolation to such a low mobility value u as was found for the polymer investigated here is not possible, but the shape of the u - n dependence shows that the value $1 \cdot 10^{-5} - 2 \cdot 10^{-5}$ could be assumed by the mobility of the segment only at a very high molecular weight of the segment (order of magnitude 10^3).

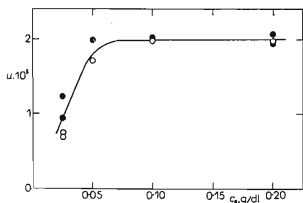


FIG. 1

Dependence of Mobility of Fraction IV on Concentration of Poly(2-Hydroxyethyl Methacrylate)

●, ○ Ascending or descending boundary at ionic strength 0.6.

The results of further estimates depend to a certain extent on the assumed shape of the segment. Noda and coworkers⁴ used for molecules of polyacrylic acid dissociated to a various degree the model of a prolated ellipsoid with a constant diameter, whose frictional coefficient is given by⁶

$$f_{es} = 6\pi\eta_0 R_0(1 - p^2)^{1/2}/p^{2/3} \ln \{p^{-1}[1 + (1 - p^2)^{1/2}]\}, \quad (3)$$

where η_0 is the viscosity of the solvent, R_0 is the radius of a sphere having the same volume as the ellipsoid, and p is the ratio of the shorter semi-axis to the longer one, $p = b/a$. If the ratio R_0 is expressed by means of the shorter semi-axis according to $(4/3)\pi R_0^3 = (4/3)\pi ab^2$, we obtain after substitution into Eq. (3)

$$f_{es} = 6\pi\eta_0 b(1 - p^2)^{1/2}/p \ln \{p^{-1}[1 + (1 - p^2)^{1/2}]\}. \quad (4)$$

According to Noda⁴, Stokes' radius of the monomer unit can be substituted for b . Its exact value is not known. Calculations will therefore be made for two values; the actual value of Stokes' radius will probably lie between them. If $f_{es} = 8 \cdot 10^{-8}$ cm and $\eta_0 = 1.8 \cdot 10^{-2}$ g cm⁻¹ s⁻¹, we obtain for the lower limit of $b = 3 \cdot 10^{-8}$ cm the value of the semi-axes ratio $p = 0.03$; this corresponds to 33 monomer units in the electrophoretic segment. For the upper limit ($b = 5 \cdot 10^{-8}$ cm) we get $p = 0.056$, *i.e.* 18 monomer units in the segment. According to this calculation, the molecules of the lowest fraction would carry 4 or 8 charges respectively (depending on b), while the number of the respective charges for the highest fraction will be 100 or 180. For higher f_{es} values given above for the other experimental conditions the charge values would be reduced according to the ratio given in Eq. (4).

If the electrophoretic segment is represented by the model of Stokes' sphere with a radius a_s for which it holds $f_{es} = 6\pi\eta_0 a_s$, we shall obtain quite reasonable values for the radius; *e.g.*, $a_s = 23.6 \cdot 10^{-8}$ cm for 0.2M salt solution and $c_p \geq 0.1$ g/dl.

In order to estimate the number of monomer units in a spherical electrophoretic segment, we shall calculate the molecular weight of the polymer with a radius of gyration equal to the radius a_s calculated above. The ratio $(\bar{s}_0^2/M)^{1/2}$ for poly(2-hydroxyethyl methacrylate) in 0.2M-Mg(ClO₄)₂ at 4°C is¹ $0.215 \cdot 10^{-8}$, so that to the radius of gyration $(\bar{s}_0^2)^{1/2} = 23.6 \cdot 10^{-8}$ corresponds a molecular weight of $12 \cdot 10^3$. According to this estimate, the electrophoretic segment contains approximately 90 monomer units, which is a result which by its order of magnitude fits in with that obtained for the ellipsoidal segment.

With respect to the character of the above calculations, all numerical results should be taken only as estimates within the order of magnitude. Within the range of the molecular weights used the charge values thus estimated for both the ellipsoidal and spherical electrophoretic segment vary over an interval from 1 to 100 charges per macromolecule.

The system poly(2-hydroxyethyl methacrylate)-perchlorate is not the most suitable one for studying the interactions of ions with undissociable polymers by the method of free electrophoresis. This paper should therefore be regarded as an introduction to a more detailed investigation of more appropriate water-soluble polymers, for which there will be more freedom in the choice of salts and of the concentration ranges. We believe, however, that further investigation will bring about no important changes in the qualitative conclusions concerning the preferential binding of the anion to the polymer and the extent of this binding.

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