A specific effect of alkali-metal iodides and thiocyanates on the viscosity of solutions of poly(methacrylic acid) in methanol

J. Horský, V. Petrus and M. Bohdanecký
Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6, Czechoslovakia
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The solution properties of poly(methacrylic acid) (PMA) in methanol are specifically affected by thiocyanates and iodides of alkali metals. The relative decrease in the reduced specific viscosity of PMA in dilute methanolic solutions due to KSCN depends only on the ratio of concentrations of polymer and salt, and is independent of temperature and polymer molecular weight. With copolymers of methacrylic acid and 2-hydroxyethyl methacrylate, the effect is weaker.

(Keywords: poly(methacrylic acid); alkali-metal salts; methanol; specific interactions; viscosity behaviour)

INTRODUCTION

In the previous paper dealing with the solution properties of poly(methacrylic acid) (PMA) in methanol[1], a specific effect of alkali-metal salts on the viscosity of these solutions was briefly mentioned. Here we present detailed experimental results and discuss the role of ions, temperature, polymer molecular weight and the esterification of carboxylic groups. The conclusions are compared with those found recently for poly(acrylic acid) in methanol[2].

EXPERIMENTAL

The preparation of fractions of poly(methacrylic acid) (PMA) and non-fractionated samples of copolymers of methacrylic acid (MA) and 2-hydroxyethyl methacrylate (HEMA) has been described elsewhere[1,3]. Solvents and salts were P.A. quality. The water content in methanol (estimated by the K. Fischer method) was lower than 0.1%. The concentration of KSCN solutions was checked by potentiometric titration with mercury perchlorate.

Molecular weights of PMA were calculated from the intrinsic viscosities (in $\mathrm{cm^3\,g^{-1}}$) in methanol (with 5×10^{-4} M HCl) according to the equation[1] $[\eta]=0.224M^{0.679}$. The molecular weight of MA–HEMA copolymer CO48 (*Table 1*) was determined by means of the Archibald approach-to-equilibrium method, and also from the sedimentation coefficient s_0 and intrinsic viscosity $[\eta]$ (in methanol at 25°C) according to the Mandelkern–Flory equation:

$$s_0[\eta]^{1/3}M^{-2/3}=\Phi_0^{1/3}P^{-1}(1-v_2\rho_0)/(\eta_0N_{\mathrm{A}}) \qquad (1)$$

with $s_0=9.6\times10^{-13}\,\mathrm{s}$, $(1-v_2\rho_0)=0.438$, $[\eta]=34\,\mathrm{cm^3\,g^{-1}}$, $\eta_0=5.64\times10^{-3}\,\mathrm{g\,cm^{-1}\,s^{-1}}$, $\Phi_0^{1/3}P_0^{-1}=1.08\times10^7$, and where N_{A} is the Avogadro number.

Viscosity measurements were made as described in ref. 1. Methanol and methanolic solutions of hydrogen chloride and alkali-metal salts were used as solvents. The characteristics of the samples are collected in *Table 1*.

RESULTS AND DISCUSSION

The concentration dependence of reduced viscosity, η_{sp}/c, of PMA in methanol displays a minimum typical of dilute solutions of polyelectrolytes (*Figure 1*, curve A). The reduced viscosity, however, rises at very low polymer concentrations; this is why the polyelectrolyte effect has not been noticed in previous papers dealing with this system. The minimum can be suppressed by a very low concentration of hydrogen chloride (5×10^{-4} M). As shown by *Figure 1* (curve B), plots of η_{sp}/c vs. polymer concentration c are linear, and the Huggins coefficients k_{H} are in the usual range for uncharged polymers (*Table 1*).

We also tried to suppress the polyelectrolyte effect by adding low molecular weight salts soluble in methanol (LiCl, NaI, KI, KSCN, NH_4SCN) at a concentration $C_{\mathrm{s}}\simeq0.2$ M. Ammonium thiocyanate had a similar effect to hydrogen chloride. In the presence of LiCl, the viscosity was not constant but decreased with time in an irreproducible way.

The effect of other salts was quite different and unexpected. All of them removed the minimum but the plots of η_{sp}/c vs. c deviated from linearity in the sense opposite to that for pure methanol. As shown by *Figure 1*, the curves for iodides and potassium thiocyanate decreased with decreasing polymer concentration (at constant salt concentration, C_{s}) so steeply that one would expect them to drop almost to $\eta_{\mathrm{sp}}/c\simeq0$ at a very low, but finite, polymer concentration. Before reaching this region, the solution became turbid due to phase separation.

The reduced viscosity values before phase separation were very low. By comparing them with the intrinsic viscosity, $[\eta]_\theta$, corresponding to the unperturbed dimensions in methanol, one can assess the degree of coiling of the chain. For example, for PMA A-1-2 ($M=1.85\times10^6$) in 0.23 M KSCN, the value of η_{sp}/c at $c=6.3\times10^{-4}\,\mathrm{g\,cm^{-3}}$ is $26\,\mathrm{cm^3\,g^{-1}}$ while $[\eta]_\theta=182\,\mathrm{cm^3\,g^{-1}}$ as estimated according to ref. 1. The ratio $(\eta_{\mathrm{sp}}/c)/[\eta]_\theta=0.14$ gives the evidence of hypercoiling.

The effect of KSCN was investigated in more detail. It

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Table 1 Characteristics of polymers

Polymer	x_H[a]	$M\times10^{-4}$ [b]	$[\eta]$[c] ($cm^3\,g^{-1}$)	k_H[c]
Poly(methacrylic acid), PMA				
A-1-2	–	185	403	0.33
A-1-5	–	66	201	0.26
A-1-6	–	41	145	0.26
A-2-1	–	51	169	0.26
A-2-2	–	16	76	0.29
Copolymers of MA and HEMA				
CO73.5	0.265	–	41	0.37
CO48	0.520	9.1[d], 9.8[e]	34	0.44
CO25	0.750	–	27	0.49
CO12.6	0.874	–	27	0.51

[a] Mole fraction of 2-hydroxyethyl methacrylate (HEMA)
[b] From $[\eta]$
[c] In 5×10^{-4} M methanolic HCl at 25°C
[d] By the Archibald method
[e] From $[\eta]$ and s_0 according to equation (1)

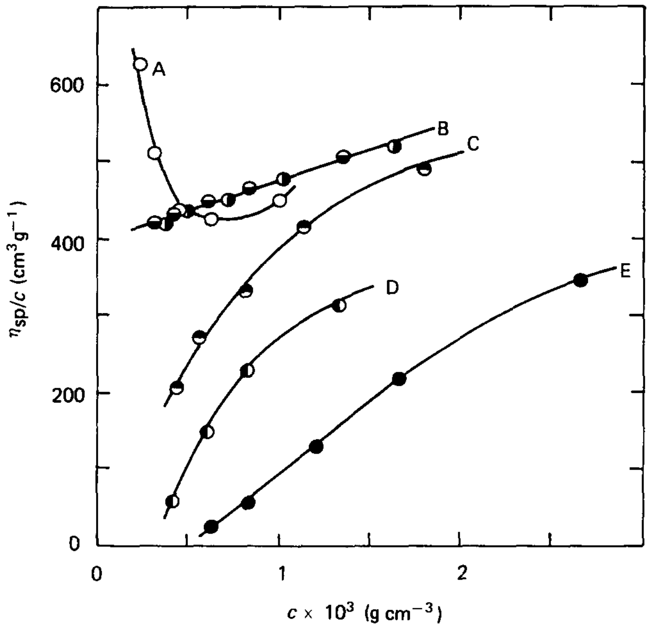

Figure 1 The effect of low molecular weight electrolytes on the viscosity of poly(methacrylic acid) in methanol at 25°C. Polymer: fraction A-1-2. Solvents: methanol (○); methanolic solutions of HCl (0.0005 M) (◑), NH_4SCN (0.21 M) (◒), NaI (0.20 M) (◐), KI (0.20 M) (◓), and KSCN (0.23 M) (●)

turned out that the best way for data treatment is to plot the ratio of the reduced viscosities of the polymer in methanol with added salt and in methanol with hydrogen chloride (hereafter called 'viscosity ratio') vs. monomer unit/salt molar ratio. Reduced viscosities in methanol with hydrogen chloride for a given polymer concentration were calculated by means of the Huggins equation:

$$\eta_{sp}/c=[\eta]+k_H[\eta]^2c \qquad (2)$$

with $[\eta]$ and k_H from *Table 1*.

In spite of some scatter of the data points, particularly noticeable in *Figure 3*, the values of viscosity ratio depend only on the monomer unit/salt molar ratio and are independent of the absolute concentration of KSCN, the polymer molecular weight and temperature (*Figures 2–4*). With copolymers of MA and HEMA, the effect of KSCN depends on the copolymer composition (mole fraction, x_H, of HEMA units). It is almost negligible at $x_H=0.87$ and becomes pronounced as x_H decreases. At $x_H=0.25$ it is comparable to the effect observed with PMA (*Figure 4*).

By comparing different salts, one finds that their effect on the viscosity of PMA in methanol is mainly governed by the cations (compare KSCN and NH_4SCN, KI and NaI) although the anions (CNS^-, I^-) also play some role. The effect of anions may be indirect and due to an incomplete dissociation of alkali-metal salts in methanol, which is indicated by measurements of conductivity and refractive index[4,5].

The unusual shape of the dependences of reduced viscosity on polymer concentration can be qualitatively

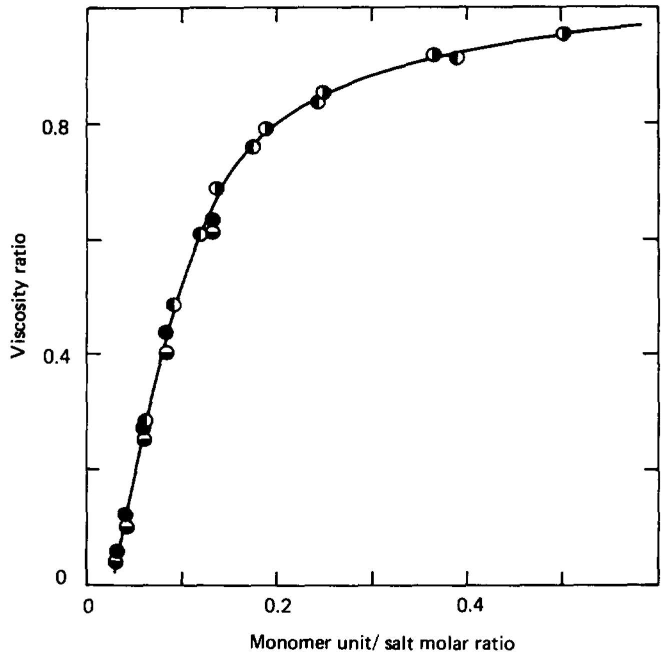

Figure 2 The effect of salt concentration on the relative decrease of reduced viscosity of PMA in methanolic solution of KSCN. Viscosity ratio is the ratio of reduced viscosities in methanol with KSCN and in methanol with HCl (5×10^{-4} M). Concentration of KSCN 0.23 M (●), 0.12 M (◒), 0.04 M (◐), and 0.02 M (◑). Polymer: fraction A-1-2 at concentrations $(2.5\text{–}25)\times10^{-4}\,g\,cm^{-3}$

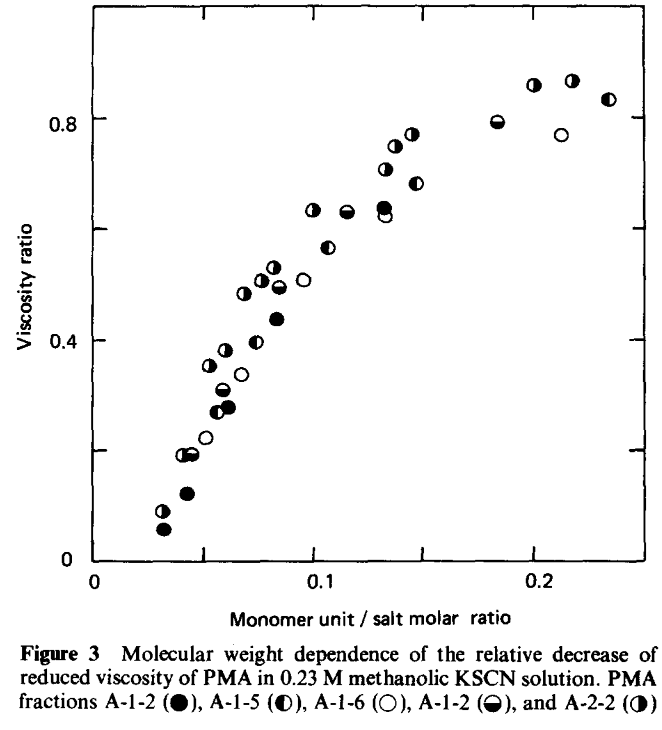

Figure 3 Molecular weight dependence of the relative decrease of reduced viscosity of PMA in 0.23 M methanolic KSCN solution. PMA fractions A-1-2 (●), A-1-5 (◐), A-1-6 (○), A-1-2 (◒), and A-2-2 (◑)

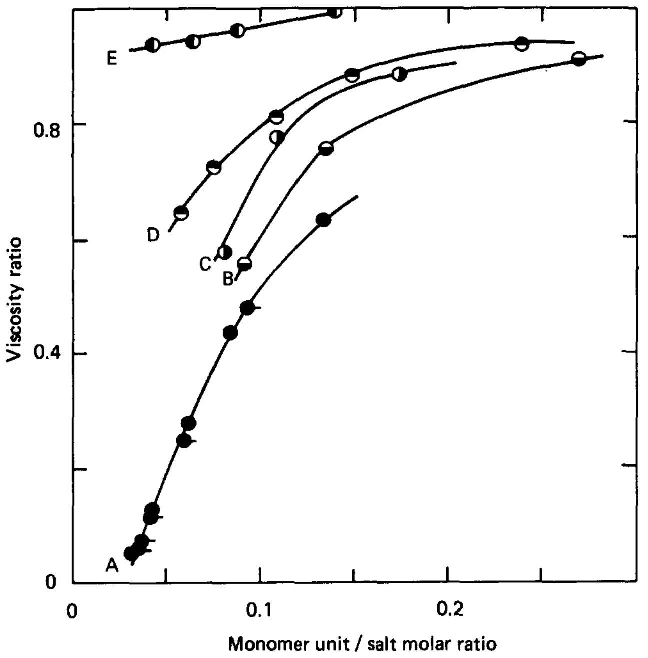

Figure 4 The effect of temperature and esterification on the relative decrease of reduced viscosity of PMA in 0.23 M methanolic KSCN solution. Polymers: (at 25°C) CO12.6 (◐), CO25 (◓), CO48 (◑), CO73.5 (◒), PMA A-1-2 (●); (at 45°C) PMA A-1-2 (●-)

explained by assuming that the cations associate with the COOH groups of the PMA chain. If the total salt concentration is kept constant and the polymer concentration is decreased, the salt concentration in the free solvent and, hence, the occupancy by cations of polymer chains will be increased.

The phase separation at low polymer concentrations (mentioned above) lends support to the idea that the solvent power of methanol for the associates is important for the effects studied and that it is the weaker the higher the relative chain occupation. Consequently, the chains shrink and the viscosity decreases as the polymer concentration is lowered. As illustrated above by the value of $(\eta_{sp}/c)/[\eta]_\theta$, the degree of shrinking may be very high.

In the association with cations, the carboxyl groups of PMA can be in the undissociated or dissociated form, the latter being due to the action of the solvent or of the cation. The fraction of dissociable groups is lower in MA–HEMA copolymers. As shown by *Figure 4*, the viscosity ratio values at the same monomer unit/salt molar ratio are higher the higher is the content of HEMA units. This indicates (but does not confirm) that the carboxylic groups with dissociable hydrogen atoms are essential for the interaction with the cations.

When analysing the viscosity data of polymers in mixed solvents such as salt solutions, one should consider the fact that the intrinsic viscosity in such a system need not be simply related to the size of macromolecules if strong preferential solvation takes place[6].

When calculating the reduced viscosity, it is usual to employ the viscosity of the pure mixed solvent, although one should use the value for the mixed solvent whose composition corresponds to the equilibrium with the polymer. Neglect of this difference may introduce an error. In order to check this factor, we estimated the solvent viscosity η_s by means of the Jones–Dole equation:

$$\eta_s = \eta_0(1 + A\sqrt{C_s} + BC_s) \tag{3}$$

with constants A and B estimated from the flow times of methanolic KSCN solutions, and used it to calculate a more correct value of η_{sp}. It turned out that the very low viscosity ratio values observed with our systems could be obtained only if several cations were associated with one monomeric unit. Since association of one cation with several monomeric units is more probable, the effect discussed in ref. 6 cannot account for low values of the viscosity ratio.

The ionization of poly(acrylic acid) (PAA) in methanol has recently been investigated by several methods[2]. The results were different if lithium or sodium methoxides were used for neutralization. A transition from the coil-like to compact conformation was found to set in, at a certain degree of ionization, with sodium methoxide, but was absent with lithium methoxide. The conformational transition was assigned to the solvent power of methanol being lower for more dissociated PAA molecules, and the specific effect of cations was ascribed to different solvation by methanol.

Our results bear some resemblance to those of ref. 2. They confirm the specific interaction of ions with the polyacids in methanol and the existence of a hypercoiled chain conformation. The role of ionization of the polyacid, however, seems to be less clear now because our measurements were carried out without any (apparent) neutralization.

A practical consequence follows from the present study. The shape of the dependences in *Figures 2–4* is such that in a certain range of the monomer unit/salt molar ratio (particularly if larger than 0.2), the nonlinear dependence of η_{sp}/c on c at a constant salt concentration may escape notice. The intrinsic viscosity obtained by extrapolation will then be low and significantly wrong.

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