The Viscometric Methods in the Investigation of the Polyacid–Polybase Interpolymer Complexes

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SYNOPSIS

Two viscometric methods in the investigation of interpolymer complexes are presented. It has been shown that a presentation of the reduced viscosity ratio (experimental to ideal value) of a mixture of a polyacid with a nonionic polymer at constant total concentration as a function of the polymer mixture composition gives a better insight into the interpolymer association than a presentation of the specific viscosity at constant polyacid concentration as a function of the unit molar ratio. The formation of an expanded structure interpolymer complex is more easily revealed by the former procedure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Interpolymer complexation between complementary polymers through hydrogen bonding has recently attracted a great interest.[1,2] Viscometry measurements[3-15] are among the most frequently used methods for the study of these complexes.

Due to the acid-base character of the hydrogen bonding interaction the obtained results concerning these complexes are usually plotted as a function of the unit molar ratio, [polybase]/[polyacid], keeping constant the polyacid concentration, according to an acid-base titration procedure. The viscometric results are presented usually by plotting either the reduced viscosity, η_{sp}/c,[3-5,7] or the specific viscosity, η_{sp},[8,9,12-14] at constant polyacid concentration, as a function of the molar ratio. According to another procedure, the difference, $\Delta\eta_{sp}$, between the experimentally determined specific viscosity, $(\eta_{sp})_{exp}$, and the calculated value, $(\eta_{sp})_{calc} = \Sigma\eta_{spi}$, has been plotted as a function of the polymer mixture composition.[6] This procedure presents the deviation of the specific viscosity of the polymer mixture from an "ideal" value calculated by application of the rule of additivity considering the absence of any interactions.

Two of us have recently[11] plotted the relative deviation between the experimentally determined reduced viscosity, $(\eta_{sp}/c)_{m,exp.}$ and the calculated "ideal" one, $(\eta_{sp}/c)_{m,id.}$, as a function of the weight fraction of the polyacid, keeping the total polymer concentration constant. This "ideal" value is based on the additivity rule of the specific viscosities of the two pure polymers properly modified in order to take into account the polyelectrolyte effect exhibited by the polyacid. A slightly different version is to plot the reduced viscosity ratio, $r_{\eta_{red}} = (\eta_{sp}/c)_{m,exp}/(\eta_{sp}/c)_{m,id}$ versus the polyacid weight fraction, W_{PAA}.[15]

In this work dilute aqueous solutions of mixtures of polyacrylic acid (PAA) with two polybases; namely, polyethyleneglycol (PEG) and polyacrylamide (PAAm) have been viscometrically investigated. More precisely, we focus our attention on the comparison of the two viscometry procedures.

EXPERIMENTAL

The PAA sample used has been described elsewhere[10] and its molecular mass equals to 1.3 × 10⁵. The PEG sample, a product of Fluka, was purified by precipitation with hexane from chloroforme solution. Its molar mass has been determined viscometrically in water[16] and has been found to equal 4.25 × 10⁴. The PAAm sample was synthesized in a 5% water solution of acrylamide (Sigma) using hydrogen peroxide as initiator[17] at 50°C. It was pre-

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cipitated in methanol, dissolved in water and repre-
cipitated, then dried in vacuum for two days at 35°C.
Its molecular mass has been determined viscometr-
ically in water[18] and has been found to equal 1.06
× 10⁵.

Water used for the preparation of the solutions
was deionized by an ion-exchange resin and purified
by a Millipore Norganic cartridge equipped with a
0.45 μm filter.

Viscosity measurements were performed with a
Cannon Ubbelhode-type viscometer at 30°C. The
solutions used were adequately dilute so that the
product $[\eta]_c$ did not exceed the critical value 0.7.[18]

RESULTS AND DISCUSSION

Figure 1 shows the variation of the specific viscosity,
η_{sp}, for the PAA/polybase (PEG, PAAm) mixtures
as a function of the molar ratio r = [PB]/[PAA];
[PB] and [PAA] are the concentrations in unit mol
L^{-1} of the polybase and of the polyacrylic acid, re-
spectively.

When r < 1, addition of PEG in the solution of
PAA results in a decrease of the specific viscosity.
Further addition of polybase, r > 1, results in a
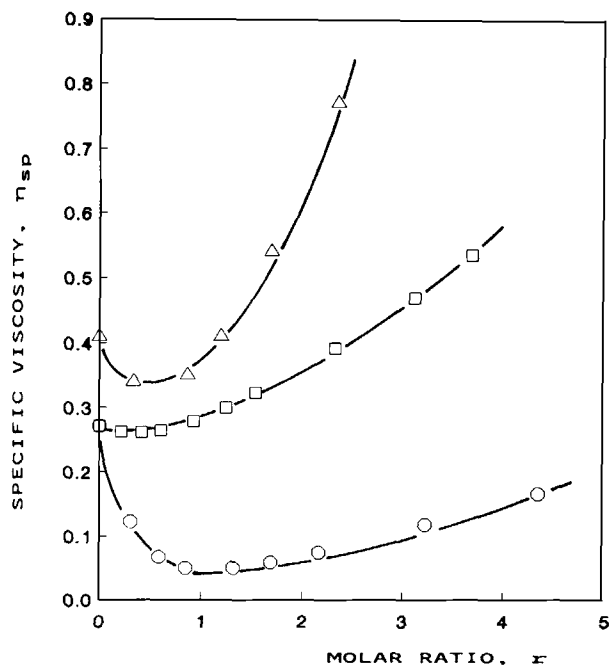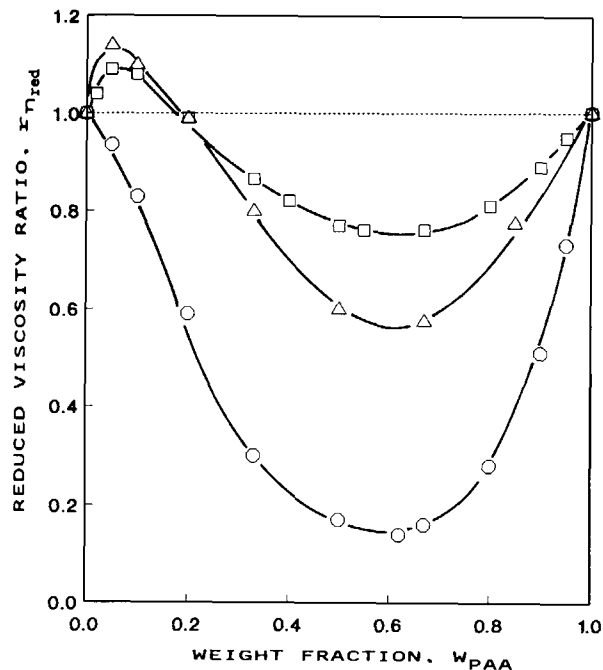steady increase in η_{sp}. This behavior has been con-

Figure 2   Variation of the reduced viscosity ratio, $r_{\eta_{red}}$,
of PB/PAA water solutions as a function of the PAA
weight fraction, w_{PAA}, at 30°C. The total concentration,
c, is constant. PB: (O) PEG, (□) PAAm, c = 3.00 × 10⁻³
g cm⁻³ (△) PAAm, c = 9.00 × 10⁻³ g cm⁻³.

sidered as typical of systems forming polymer com-
plexes.[3,4,13] The same behavior, (i.e., decrease in vis-
cosity) has been observed with PAAm, but for r < 0.5
while this decrease is now very smooth. Nevertheless
we observe a more pronounced decrease when the
concentration of the solution is higher ([PAA]
= 4.0 × 10⁻² instead of 1.33 × 10⁻² unit mol L^{-1}).
The above described behavior could be summarized
as follows. In the PEG/PAA mixture a strong 1 : 1
complex is evidenced. In the PAAm/PAA mixture
a weak 1 : 2 complex seems to be favored.

In Figure 2 the variation of the reduced viscosity
ratio, $r_{\eta_{red}}$, as a function of the PAA weight fraction,
w_{PAA}, for these polymer mixtures is presented. As
it is seen in this figure $r_{\eta_{red}}$ shows a pronounced neg-
ative deviation from ideal behavior ($r_{\eta_{red}}$ = 1) for
the PEG/PAA mixture suggesting the formation of
a compact structure, in agreement with the results
of Figure 1. For the PAAm/PAA mixture a smooth
positive deviation till w_{PAA} = 0.2 and then a smooth
negative deviation are observed. This behavior sug-
gests the existence of an expanded and a compact
structure depended on the polymer mixture com-
position. When the total polymer mixture concen-
tration is higher (c = 9.0 × 10⁻³ instead of 3.0 × 10⁻³
g cm⁻³) this behavior is appearing more pronounced.

Figure 1   Variation of the specific viscosity, η_{sp}, of PB/
PAA water solutions as a function of the unit molar ratio,
r, at 30°C. PB: (O) PEG, (□) PAAm, [PAA] = 1.33 × 10⁻²
unit mol L^{-1}, (△) PAAm, [PAA] = 4.00 × 10⁻² unit mol
L^{-1}.

The results obtained with the two viscometric methods lead us to the following conclusions. The presentation of the reduced viscosity ratio as a function of the polymer mixture composition appears to offer some advantages with respect to the presentation of the specific viscosity as a function of the unit molar ratio. (1) The total concentration of the polymer mixture is constant for all measurements, so that we can work in the region of dilute solutions for every composition of the mixture. (2) All composition regions of the polymer mixture are investigated. (3) It is easier to observe the weak interactions by the appearance of smooth deviations. (4) Any interaction leading to the formation of an expanded structure is easily revealed by the appearance of a positive deviation.

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