

## Viscometric Behaviour of Barium, Lead and Copper Polymethacrylates in Acidic Medium

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**Summary:** The viscosity behaviour of barium, lead and copper polymethacrylates in 1.0 M hydrochloric acid at 30 °C has been reported for various concentrations. The concentration range studied conform to the viscosity behaviour explained on the basis of ionic radii. Barium polymethacrylate has lower viscosity than that for lead and copper polymethacrylates.

### Introduction

The presence of random coil polymers in a flowing solvent cause a viscous drag, which is termed as viscosity function [1]. The solution properties of polymers show very complex behaviour depending upon the nature of side groups and the specific interactions between the monomer units [2]. Poly (methacrylic acid) (PMAA) acts as a polyelectrolyte due to the interaction between the charged groups of ionized acid and has been investigated by Arnold and Caplan [3].

In the present work different (Ba, Pb and Cu) salts of PMAA have been synthesized by neutralization of the carboxylic group with the respective metal ions. The viscometric behaviour of these polymeric salts at different concentrations have been reported and discussed in light of the metal atoms introduced in the parent polymer.

### Results and Discussion

The values of relative viscosities at different concentrations have been plotted in figure 1. The increase in viscosity with concentration can be explained on the basis that more molecules of solute (polymers) are added into the solution which enhance the interaction between solute and solvent molecules. It is apparent from figure 1 that the viscosity values at 0.2 g/100 ml of the solution are in the order of CuPMA > Pb > PMA > BaPMA. This behaviour is in accordance with the explanation reported by Marcus [7]. According to him the ions of smaller ionic radii have greater viscosities than those with larger ionic radii. In the present study the bivalent copper ion has ionic radius equalling 0.72 Å while the bivalent ions of lead and barium have ionic radii of 1.20 Å and

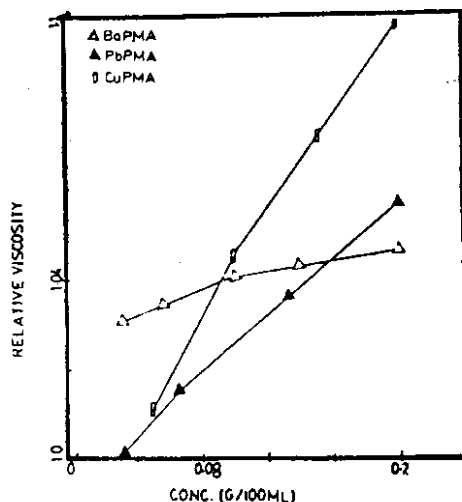


Fig. 1: The plot of relative viscosities at different concentrations.

1.34 Å respectively [8]. The hydrogen bonded structure of the solvent (HCl) does not allow the  $Ba^{+2}$  ion to enter the hydration sphere, thus disrupting the hydrogen bonding and consequently decreasing the viscosity.

The ion - solvent interaction (B) and ion - ion interaction (A) coefficients were calculated following Jones and Dole equation [9] by using the data on the slopes and intercepts from the plots of  $(\eta/\eta_0)/C^{1/2}$  versus  $C^{1/2}$  given in figure 2. The B coefficients representing the order or disorder introduced in the solute - solvent system are -0.20, 0.44 and 0.74 for BaPMA, PbPMA and CuPMA respectively. The negative B coefficient value for BaPMA confirms that the barium ion in the polymer matrix decreases

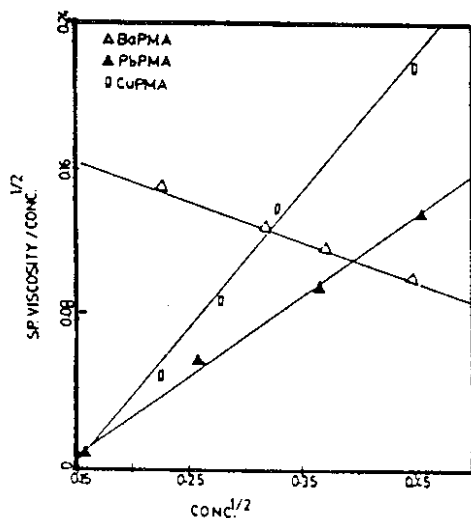


Fig. 2: The plots for the determination of interaction coefficients.

the viscosity by depolymerizing the associated HCl medium. The values of A coefficient are 0.19, -0.053 and -0.11 for BaPMA, PbPMA and CuPMA respectively. These values indicate that ion-ion interaction is small in the acidic solutions of PbPMA and CuPMA resulting in enhanced ion-solvent interactions. However, a reverse trend is observed for BaPMA due to the larger ionic radius of  $Ba^{+2}$  ion.

The limiting viscosity number of solutions is determined by applying Kraemer or Huggins equations [10]. In the present work the changes in reduced viscosity with concentration follow the Huggins equation. The intrinsic viscosity values of 3.37, 3.76 and 3.33  $dm^3/g$  were obtained from figure 3 using the Kraemer's equation [10].

$$\ln \eta_{rel}/C = [\eta] - K_k[\eta]^2 C$$

where;  $K_k$  = Kraemer's constant,  $C$  = concentration in g/100 ml,  $\eta_{rel}$  = relative viscosity and  $[\eta]$  = intrinsic viscosity.

It is an established fact that intrinsic viscosity is proportional to the molar mass of the solute [11]. As the molecular weight of lead methacrylate units is higher than that for barium and copper methacrylate units the intrinsic viscosity for PbPMA is greater than BaPMA and CuPMA.

It is desirable from a practical point of view in the viscosity related studies of polymers to estimate

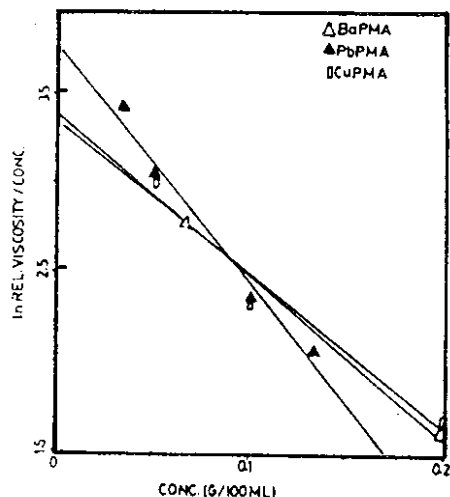


Fig. 3: Plots for the determination of intrinsic viscosities.

the concentration where transition from semi-dilute to concentrated solution takes place [12]. It is denoted as  $C^{**1at}$

$$C^{**1at} = 1/[\eta]$$

The concentrations at which the acidic solutions for MPMA are completely saturated with polymer coils are 0.297, 0.266 and 0.30 g/ml for BaPMA, PbPMA and CuPMA respectively. These values point towards the possibility of polymer coil overlapping on further addition of polymer to the solution.

These studies reveal that the viscosities of polymeric salts depend upon the ionic radius of the metal ion chemically bound to the polymer backbone.

## Experimental

### Synthesis

25% w/v methacrylic acid (MMA) in dried methanol was polymerized [4] using 0.01% w/v azo-bis isobutyronitrile at 60 °C for 120 minutes. The reaction mixture was poured in constantly stirred diethyl ether to obtain PMAA of number average molecular weight 15329.

The methanolic solutions of PMAA and sodium hydroxide were mixed in equimolar ratios to precipitate sodium polymethacrylate (NaPMA). This was then dissolved in water and poured into the

stirred aqueous solutions of the respective metal salts ( $\text{BaCl}_2$ ,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{CuCl}_2$ ) in stoichiometric quantities to obtain the respective metal polymethacrylate [4]. The samples were dried for 24 hours at  $30^\circ\text{C}$  in a vacuum oven and stored in a desiccator.

#### Characterization

The polymers were characterized by infrared spectroscopy using a Hitachi 270-50 infrared spectrophotometer. The symmetric and antisymmetric peaks in the region  $1600\text{-}1530\text{ cm}^{-1}$  and the absence of peak at  $1640\text{ cm}^{-1}$  confirmed the formation of the polymers.

The metal content of these samples was estimated by employing atomic absorption spectrophotometry, inductively coupled plasma spectrometry and potentiometry. The polymers were digested with a mixture of perchloric acid and nitric acid before analysis. Experimentally determined metal contents were 44.25 (44.69), 54.61 (54.91) and 26.64 (27.26) percent for BaPMA, PbPMA and CuPMA respectively. The values in the brackets are the theoretically calculated values for the respective metals.

#### Measurement of flow rates

Different solutions of metal polymethacrylates (MPMA) were prepared in 1.0 M HCl for the determination of the flow rates. Solution concentrations were 0.05 g/100 ml to 0.2 g/100 ml. The viscosities were determined at 303 K using a Ubbelohde viscometer with flared ends. The solvent flow times of above 100 secs were maintained to

avoid kinetic energy corrections [5]. The intrinsic viscosities were evaluated from the data obtained at a minimum of three concentration [6].

#### Measurement of density

Solution densities were measured using a density meter model DMA 60 of Anton Paar, Austria.

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