

Conductivity and relaxation effect of alkali polymethacrylates in alkali bromide solutions*

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Abstract. The electric conductivity of alkali polymethacrylates in aqueous solutions of alkali bromides with concentrations varying from 0.001 mol/l to 0.1 mol/l was measured. From a comparison of the conductivities of different alkali salts (Li, Na, K) the relaxation correction on the mobility of the polyion and of the counterions was estimated by use of the method of Möller et al. This correction lowered the mobilities by a factor of about one half. Relaxation effects of similar magnitude have been derived from the dispersion of the conductivity of other linear polyelectrolytes in the megacycle range.

1. Introduction

The electric conductivity and transference of solutions of simple ions can in principle be interpreted from the limiting ionic conductivities, the electrophoretic retardation and the relaxation effect as caused by the ionic atmosphere.

For highly charged colloid ions the calculation of the electrophoretic mobility is much more difficult. As compared with small ions a massive polyelectrolyte ion distorts the hydrodynamic flow pattern and the electrical double layer to a high degree (*Wiersema, Loeb and Overbeek*¹). For coil-like polyelectrolytes the situation is still more complicated, because the small ions penetrate into the coil and can move within it, resulting in a strong interaction between the coil and the counterions.

Thus it is easy to understand that a complete theory of the electrophoresis of coil-like polyelectrolytes does not yet exist. Several attempts have been made, starting from the porous sphere model, by *Hermans and Fujita*², *Hermans*³, *Napjus and Hermans*⁴ and by *Overbeek and Stigter*⁵.

Other authors regarded the polyion as a randomly kinked cylinder and used *Henry's*⁶ equation for the motion of a charged cylinder (*Overbeek and Stigter*⁵, *van Geelen*⁷ and *Nagasawa et al.*⁸). These theories include the electrophoretic retardation, but the relaxation effect is left out of consideration.

Attempts to calculate the relaxation effect for the porous sphere have been made by *Longworth and Hermans*⁹ and by *Imai and Iwasa*¹⁰. Of these, only the latter attempt leads to a quantitative, although rather rough estimate of the relaxation field. Recently *Stigter*¹¹ carried out calculations of the relaxation effect of randomly oriented cylinders. Some of our data have been used by *Stigter* for comparison with his theory.

* Dedicated to Professor E. Havinga as a token of our appreciation for his widespread achievements.

¹ P. H. Wiersema, A. L. Loeb and J. Th. G. Overbeek, *J. Colloid Interface Sci.* **22**, 78 (1966).

² J. J. Hermans and H. J. Fujita, *Proc. K. Ned. Akad. Wet.* **B58**, 182 (1955).

³ J. J. Hermans, *J. Polym. Sci.* **18**, 527 (1955).

⁴ P. J. Napjus and J. J. Hermans, *J. Colloid Sci.* **14**, 252 (1959).

⁵ J. Th. G. Overbeek and D. Stigter, *Recl. Trav. Chim. Pays-Bas* **75**, 543 (1956).

⁶ D. C. Henry, *Proc. R. Soc. London* **A133**, 106 (1931).

⁷ B. van Geelen, *Electrophoresis of polymethacrylic acid*, Thesis, Utrecht, The Netherlands, 1958.

⁸ M. Nagasawa, I. Noda, T. Takahashi and N. Shimamoto, *J. Phys. Chem.* **76**, 2286 (1972).

⁹ R. Longworth and J. J. Hermans, *J. Polym. Sci.* **26**, 47 (1957).

¹⁰ N. Imai and K. Iwasa, *Isr. J. Chem.* **11**, 233 (1973).

¹¹ D. Stigter, *J. Phys. Chem.* **82**, 1417, 1424 (1978).

Accurate data on the electrical transport in polyelectrolyte solutions are scarce. We therefore decided to obtain experimental data on the mobility of polyions and counterions. We interpret these data using the semiempirical method developed by Möller et al.¹² for an estimate of the relaxation effect, and applying a refined form of Henry's⁶ equations for cylinders. In the present paper we report the results of conductivity measurements of solutions of poly(methacrylic acid) (PMA) partially neutralized with LiOH, NaOH or KOH, in the presence of the corresponding alkali bromides; and with Möller's method we determine the values of the relaxation correction. Bromides were used to allow higher accuracy in the parallel *Hittorf* transference measurements. We shall use some results of these *Hittorf* measurements¹³ to prove that an assumption essential for Möller's method is justified. This assumption is: independence of the mobilities of the PMA polyion and of the co-ions from the nature of the alkali counterions.

2. Materials and methods

2a. Nitrogen

Tank nitrogen was carefully freed from oxygen (O_2 content < 1 ppm), carbon dioxide, water and ammonia.

2b. Water

Distilled water was redistilled from a quartz vessel, with a quartz condenser. Bubbling nitrogen through the redistilled water overnight reduced the conductivity to 1 to $2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. It remained at this level during several days. The purified water was stored in a closed Pyrex flask.

2c. Poly(methacrylic acid) (PMA)

Poly(methacrylic acid) was prepared by free radical polymerization in 4.3% aqueous solution, 0.05 mol/l in H_2SO_4 at 75°C for 5 h, using 1.6% H_2O_2 as the initiator (Katchalsky and Blauer¹⁴).

The product was divided into three fractions of about equal size by precipitation with methyl ethyl ketone. Only the middle fraction was used for the experiments. After prolonged electro dialysis (De Bruyn and Troelstra¹⁵) in the dark (Völker¹⁶) against purified water the middle fraction was freeze dried. The yield of this fraction was about 25%.

The PMA content of the product was determined by potentiometric titration with 0.1 mol/l NaOH and was found to be 93.8%. This agreed quite well with a water content of 6.1% determined by Karl Fisher titration. After ashing a small amount of SiO_2 ($\ll 0.1\%$) was found, possibly stemming from the stirring in the electro dialysis cell. The sulphate content was below detection level.

The molar mass was $270,000 \text{ g mol}^{-1}$, as determined by light scattering in 0.002 mol/l HCl (Katchalsky and Eisenberg¹⁷).

2d. Carbonate free alkali hydroxides

Carbonate free alkali hydroxides were prepared using the insolubility of Na_2CO_3 in concentrated NaOH (Kolthoff and Sandell¹⁸) and using the amalgam method (Knobel¹⁹) for LiOH and KOH.

2e. Other chemicals

Sodium bromide (Union Chimique Belge, pour analyse), potassium bromide (Riedel-de Haën, für Analyse), lithium bromide, anhydrous (British Drug Houses) and potassium chloride (UCB, pour analyse) were used without further purification. They were dried only; first overnight at 120°C and then slowly heated up to 600°C (NaBr and KBr) or

400°C (LiBr) and held at this temperature during 30 minutes (Jervis et al.²⁰) in a stream of purified nitrogen.

2f. Conductivity measurements

For our conductivity measurements we used an a.c. bridge method essentially based on the design of Jones and Josephs²¹ and Shedlovsky²². For a good survey of the technique and of the precautions that have to be taken, we refer to Hague²³.

The resistances of the bridge were calibrated (accuracy 0.005%) with direct current at the Physical Laboratory of the University of Utrecht.

The influence of the a.c. frequency on the balancing of the bridge was tested with carbon black resistances, which have a very low reactance. Up to 50 000 Ω (0.5 to 4 kHz) and up to 100 000 Ω (0.5 to 2 kHz) the whole bridge set up was proved to be accurate within 0.01%.

The temperature of the oil bath was kept at 25.00°C with a drift of at most 0.001 K in 30 minutes.

Jones' conductivity cells (Jones and Bollinger²⁴) type M were used. They were calibrated with potassium chloride solutions (Jones and Bradshaw²⁵) and had a cell constant of about 12 cm^{-1} . All our results are expressed in S.I. ohm.

All measurements (0.001–0.1 mol/l) could be performed with this type of cells, the resistance ranging from 10^5 – $10^3 \Omega$. The electrodes were only very lightly platinized (Eisenberg²⁶) to prevent adsorption of PMA.

Resistances were measured at 0.5, 1, 2, 3 and 4 kHz and extrapolated to infinite frequency (f) by plotting against f^{-2} (Jones and Christian²⁷).

2g. Solutions

Solutions were prepared gravimetrically from stock solutions of salt and of PMA of various degrees of neutralization under nitrogen saturated with water vapor in half litre MacInnes flasks (MacInnes and Dole²⁸). When the whole procedure was performed with water, the conductivity was raised at most with $1 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$.

Density measurements, needed to convert molalities into molarities were performed by means of a digital precision density meter DMA 02 (Kratky, Leopold and Stabinger²⁹).

¹² W. J. H. M. Möller, G. A. J. van Os and J. Th. G. Overbeek, Trans. Faraday Soc. 57, 312, 325 (1961).

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¹⁴ A. Katchalski and G. Blauer, Trans. Faraday Soc. 47, 1360 (1951).

¹⁵ H. de Bruyn and S. A. Troelstra, Kolloid-Z. 84, 192 (1938).

¹⁶ Th. Völker, Makromol. Chem. 44–46, 107 (1961).

¹⁷ A. Katchalsky and H. Eisenberg, J. Polym. Sci. 6, 145 (1951).

¹⁸ I. M. Kolthoff and E. B. Sandel, Textbook of quantitative inorganic analysis, MacMillan, New York, 1936.

¹⁹ M. Knobel, J. Am. Chem. Soc. 45, 70 (1923).

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²¹ G. Jones and R. C. Josephs, J. Am. Chem. Soc. 50, 1049 (1928).

²² T. Shedlovsky, J. Am. Chem. Soc. 52, 1793 (1930).

²³ B. Hague, Alternating current bridge methods, Pitman & Sons, London, 1959.

²⁴ G. Jones and G. M. Bollinger, J. Am. Chem. Soc. 53, 411 (1931).

²⁵ G. Jones and B. C. Bradshaw, J. Am. Chem. Soc. 55, 1780 (1933).

²⁶ H. Eisenberg, J. Polym. Sci. 30, 47 (1958).

²⁷ G. Jones and S. M. Christian, J. Am. Chem. Soc. 57, 272 (1935).

²⁸ D. A. MacInnes and M. Dole, J. Am. Chem. Soc. 51, 1119 (1929).

²⁹ O. Kratky, H. Leopold and H. Stabinger, Z. Angew. Phys. 27, 273 (1969).

2h. pH measurements

The pH was measured with an Ingold type 401 combined glass and 3 mol/l KCl, AgCl electrode. More experimental details can be found in *Van der Drift*³⁰.

3. Results

3a. Conductivity of the solutions

The conductivity, κ , of the solutions was determined as a function of the concentration of partially neutralized PMA at a fixed concentration of added salts. At a degree of neutralization $\alpha = 0.5$ salt concentrations of 0.001, 0.003, 0.01, 0.03 and 0.1 mol/l XBr (X = Li, Na or K) were used; at $\alpha = 0.3$ and $\alpha = 0.7$ the measurements were limited to the salt concentrations 0.003, 0.01 and 0.1 mol/l XBr (X = Na or K). The conductivity of the pure salt solutions, which serve as the solvent for the polyelectrolyte, was determined from three different preparations of the same concentration. The conductivity of the solutions was found to increase slightly faster than linearly with the PMA concentration.

3b. Equivalent conductivity of the PMA salt (XPMA)

The equivalent conductivity of the polymeric salt, Λ_{XPMA} , can be defined as the increase in conductivity of the solution over that of the XBr, divided by the equivalent concentration, αC_{XPMA} .

$$\Lambda_{XPMA} = \frac{\kappa_{\text{solution}} - \kappa_{\text{XBr}}}{\alpha C_{XPMA}} \quad [1]$$

When Λ_{XPMA} is plotted against αC_{XPMA} as in figure 1, lines with a constant slope at the lower PMA concentrations were obtained, curving downwards at higher concentrations, at least for the low concentrations of XBr.

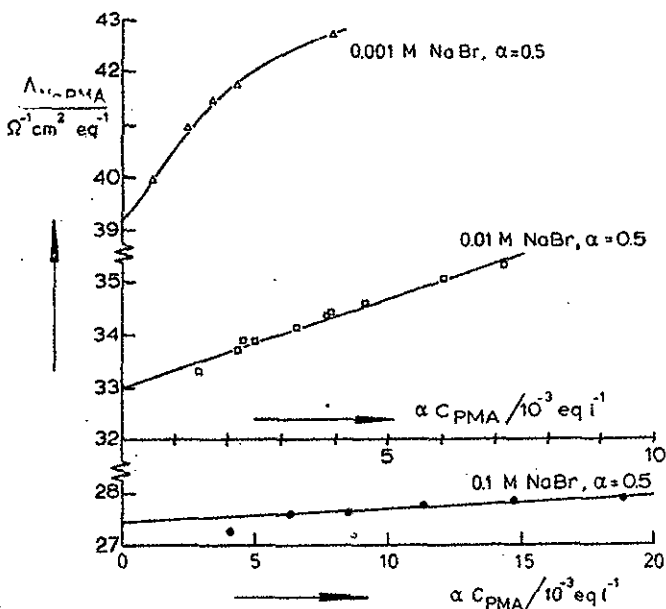


Fig. 1. Λ_{NaPMA} ($\alpha = 0.5$) at three different concentrations of NaBr (0.001, 0.01 and 0.1 mol/l). Concentrations of NaPMA (αC_{NaPMA}) are expressed in equivalents of COO^- per liter. For the calculations of the numbers in Table I only the points for the lower concentrations of PMA were used up to the concentration where clear deviations from the straight line began (2×10^{-3} eq/liter for 0.001 mol/l XBr, 4×10^{-3} eq/liter for 0.003 M XBr, all points included for higher concentrations of XBr).

The straight line parts of the plots were interpreted by writing:

$$\Lambda_{XPMA} = \Lambda_{XPMA}^0 + B(\alpha C_{XPMA}) \quad [2]$$

Λ_{XPMA}^0 is the value for zero concentration of XPMA but finite concentration of XBr. The values of Λ_{XPMA}^0 and B are calculated with the least squares method and are tabulated in Table I.

Table I Λ_{XPMA}^0 in $\Omega^{-1} \text{ cm}^2 \text{ eq}^{-1}$, and B in $10^{-6} \Omega^{-1} \text{ cm}^5 \text{ eq}^{-2}$ at various degrees of neutralization, α , and at various concentrations of XBr. Eq. refers to moles of neutralized carboxylic groups. The uncertainties in the numbers in this table are a few units of the last decimal place.

α	M_{XBr}	Λ_{LiPMA}^0	B_{LiPMA}	Λ_{NaPMA}^0	B_{NaPMA}	Λ_{KPMA}^0	B_{KPMA}
0.3	0.003			44.3	0.86	57.0	1.27
	0.01			38.31	0.29	51.43	0.33
	0.1			25.70	0.050	38.34	0.025
0.5	0.001	32.91	1.06	39.1	1.4	50.96	1.48
	0.003	29.52	0.64	36.07	0.66	47.70	0.75
	0.01	27.0	0.21	33.0	0.33	45.60	0.34
	0.03	23.7	0.2	31.5	0.12	43.9	0.23
	0.1			27.43	0.026	42.18	0.045
0.7	0.003			29.0	0.50	38.7	0.71
	0.01			26.9	0.25	37.4	0.44
	0.1			24.58	0.024	38.99	0.043

3c. Influence of H^+ -ions

At incomplete neutralization ($\alpha = 0.3, 0.5$ or 0.7) some of the carboxylic groups of the PMA will be dissociated into COO^- and H^+ . The degree of dissociation will vary with α and with the salt content of the solution, since these affect the dissociation constant. According to *Arnold* and *Overbeek*³¹ and *Leyte* and *Mandel*³² the pK of PMA is about 6 in 0.1 mol/l KCl and about 7 in 0.001 mol/l KCl, both at $\alpha \approx 0.5$. This means that there would be at most a contribution of 0.1% (usually less) of the H^+ ions to the excess of the conductivity of the solution over that of the corresponding XBr solution. Although this is not always completely negligible at the accuracy of our measurements, we refrained from making any correction for this effect since neither the concentration of the H^+ ions nor their mobility in these polyelectrolyte solutions are known accurately. Moreover, in our important equation [4] we use the differences between conductivities and the effects of H^+ would cancel in these differences.

4. Interpretation and discussion

4a. Derivation of the relaxation effect from the conductivity measurements

As mentioned in the introduction we have used the method of *Möller* et al.¹² (see also *Overbeek* and *Wiersema*³³) for estimating the influence of the relaxation effect on the mobility of polyions and counterions. This method is based

³⁰ W. P. J. T. van der Drift, Electrical transport properties of alkali poly(methacrylates), Ch. 1,3, Thesis, Utrecht, The Netherlands, 1975.
³¹ R. Arnold and J. Th. G. Overbeek, Recl. Trav. Chim. Pays-Bas 69, 192 (1950).
³² J. C. Leyte and M. Mandel, J. Polym. Sci., Part A, 2, 1879 (1964).
³³ J. Th. G. Overbeek and P. H. Wiersema, in Electrophoresis (ed. M. Bier), Vol. II, Academic Press, New York, 1967.

upon the idea that the ionic atmosphere in and around a polyion is identical for counterions of the same valence and that this identity is maintained even in atmospheres distorted by the relaxation effect.

Consequently the electrophoretic retardation and relaxation effect are assumed to be independent of the kind of counterion. Furthermore since the relaxation force exerted by the ion atmosphere on the polyion must have the same value but opposite sign from the relaxation force exerted by the polyion on the ions of the atmosphere (Onsager³⁴), the relaxation effect can be described as an electric field of average value ΔX so that both polyions and counterions move in a field $(X - \Delta X)$ when X is the applied field strength. Then for both polyions and counterions the equivalent conductivity can be written as

$$\Lambda_i = (\Lambda_i^\infty - \Lambda_{i, \text{electroph.}}) (1 - \Delta X/X) \quad [3]$$

The superscript ∞ refers to infinite dilution of both polyions and small ions. ΔX is the same for any i , $\Lambda_{i, \text{electroph.}}$ is the same for all alkali counterions and Λ_{polyion} is independent of the type of alkali counterion, if the concentrations of XBr and XPMA are the same for different X's. Application of eq. [3] for two different counterions leads to the important eq. [4]

$$\Lambda_{\text{XPMA}} - \Lambda_{\text{YPMMA}} = (1 - \Delta X/X) (\Lambda_X^\infty - \Lambda_Y^\infty) \quad [4]$$

from which $\Delta X/X$ can be found.

We want to remark that eq. [4] is independent of the model chosen for the polyion (porous sphere, cylinder). Strictly speaking this theory is valid for solutions of pure polysalt only. In the presence of (an excess of) added salt the interpretation is more difficult because in principle all ions of the solution are involved in electrophoretic and relaxation retardations. However, it has been shown experimentally (van der Drift et al.¹³) that the mobility of the co-ions is hardly affected by the presence of the polyelectrolyte. This makes it at least reasonable (cf. Möller et al.¹²) to divide the counterions into two groups, one, equivalent to the co-ions and not or hardly affected by the polyelectrolyte, and the other one equivalent to the polyion and obeying eqs. [3] and [4].

We shall return to some of the simplifying assumptions made in the theory of Möller et al. in our paper on the mobility of the polyions and its interpretation.

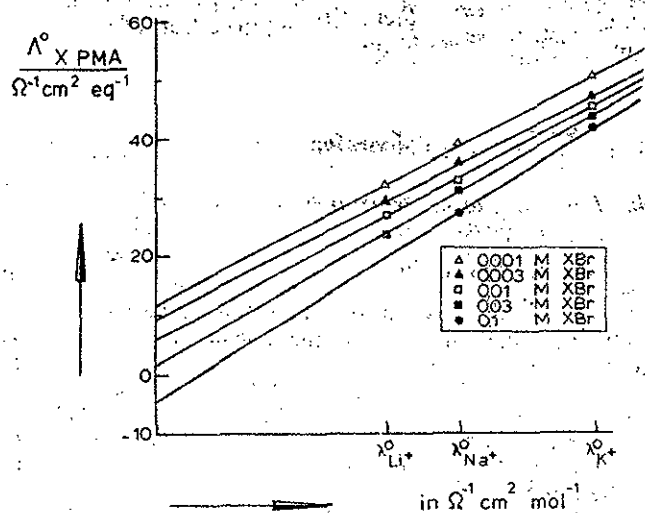


Fig. 2. Plots of $\Lambda_{\text{XPMA}}^\infty$ against the corresponding Λ_X^∞ . Degree of neutralization is $\alpha = 0.5$.

In most cases measurements have been made for three different counterions (Li, Na, K). It follows from eq. [4] that plotting of $\Lambda_{\text{XPMA}}^\infty$ against Λ_X^∞ should result in a straight line with a slope of $(1 - \Delta X/X)$. In figure 2 we show such plots for $\Lambda_{\text{XPMA}}^\infty$ taken from Table I for $\alpha = 0.5$.

In Table II the values of the relaxation factor $(1 - \Delta X/X)$ for various values of α and of $c(\text{XBr})$ are collected.

Table II Values of $(1 - \Delta X/X)$ at different degrees of neutralization α and at different bromide concentrations. Data for solutions without XBr are for XPMA concentrations of 6.25×10^{-4} eq l^{-1} (Eisenberg²⁶); $c(\text{XBr})$ is given in mol l^{-1} .

$\alpha \backslash c$	0	0.001	0.003	0.01	0.03	0.1
0.3	0.70		0.54	0.56		0.54
0.5	0.61	0.52	0.52	0.54	0.57	0.63
0.7	0.61		0.42	0.45		0.62

The data for $c(\text{XBr}) = 0$ have been calculated from Eisenberg's²⁶ measurements of salt free solutions of XPMA at a concentration of 6.25×10^{-4} eq l^{-1} .

The relaxation effect is quite large: The mobilities of the polyion and of the counterion are lowered by a factor between 0.4 and 0.6 by relaxation alone. The effect increases with increasing charge of the polyion as might be expected. The exception at $\alpha = 0.3$ and 0.1 mol/l XBr may be ascribed to the conformational transition of PMA occurring under these circumstances (Leyte and Mandel³²). The effect of a great change in electrolyte concentration is small. The slight decrease of the relaxation effect towards higher electrolyte concentrations agrees with theoretical expectations (Overbeek³⁵, Overbeek and Wiersema³³).

Conductivity measurements of other polyelectrolytes confirm the conclusion that the relaxation effect is quite large. From the data of Eisenberg and Ram Mohan³⁶ for salt free solutions of polyvinylsulphonic acid (strong polyelectrolyte, $\alpha = 1$) and its alkali salts we computed $(1 - \Delta X/X) = 0.32$.

4b. Comparison with theory and with results from high frequency conductivities

Imai and Iwasa¹⁰ have calculated the relaxation effect for fairly free-drained coils. Their results show indeed that the field near the polyion is very much lower than the applied field X . A quantitative comparison with our data is difficult.

As mentioned in the introduction Stigter¹¹ in a very important development calculated the mobility of randomly oriented cylinders including the relaxation effect. In an attempt to fit his theory to our data he concluded that the electrokinetic charge is smaller than the titration charge of PMA polyions. This would correspond to smaller relaxation corrections than the ones we have calculated. Several interpretations of this discrepancy are possible, among them: the influence of discreteness of charge or of an inhomogeneous charge distribution. It seems too early yet to draw definite conclusions about this point.

High frequency conductivity measurements offer a completely independent estimate of the relaxation effect (Debye-Falkenhagen effect, see e.g. Harned and Owen³⁷).

³⁴ L. Onsager, Phys. Z., 28, 277 (1927).

³⁵ J. Th. G. Overbeek, Philips Res. Rep. 1, 315 (1946).

³⁶ H. Eisenberg and G. Ram Mohan, J. Phys. Chem. 63, 671 (1959).

³⁷ H. S. Harned and B. B. Owen, The physical chemistry of electrolyte solutions, p. 316, 3rd ed; Reinhold, New York, 1958.

Sachs et al.³⁸ have investigated the dispersion of the conductivity of saltfree solutions of a number of linear polyelectrolytes. These experiments indicate that the relaxation effect (which disappears at very high frequency) is indeed large and of the same order as the effects found by us.

Acknowledgement

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³⁸ S. B. Sachs, A. Raziell, H. Eisenberg and A. Katchalsky, Trans. Faraday Soc. 65, 77 (1969).
