Chapter V

Effect of Salts on the Conductivity of Sodium Carboxymethylcellulose in Acetonitrile-Water Mixed Solvent Media

Introduction

We have reported the results of conductivity measurements on salt-free solution of NaCMC in acetonitrile-water mixtures in Chapter IV. Addition of low-molar-mass salts to a polyelectrolyte solution might change its conductivity behaviour dramatically and hence studies on the conductivity of polyelectrolytes in presence of a salt might help elucidate the interactions of polyelectrolytes with added salts. In this study, conductivities of NaCMC have been measured in presence of varying concentrations of sodium chloride (NaCl), potassium bromide (KBr), potassium iodide (KI) and sodium sulphate (Na_2SO_4) in acetonitrile-water mixed solvent media. These results have been analyzed to evaluate the extent of deviation from the additivity in order to assess the polyelectrolyte-salt interactions with a view to obtain information on the changes in the polyion conformation if any induced by the salt.

Experimental

Acetonitrile (E. Merck, India, 99% pure) was distilled with phosphorous pentoxide and then redistilled over calcium hydride. The purified solvent had a density of 0.76570 $gm.cm^{-3}$ and a co-efficient of viscosity of 0.3126 mPa.s at 308.15 K; these values are in good agreement with the literature values.[1] Triply distilled water with a specific conductance less than 10^{-6} $S.cm^{-1}$ at 308.15 K was used for the preparation of the mixed solvents. The relative permittivity of acetonitrile-water mixtures at the experimental temperatures were obtained with the equations as described in the literature[2] using the literature density and relative permittivity data of the pure solvents[1,3] and the densities of the mixed solvents given in Table 2 of chapter III and these are listed in Table 2 of chapter III.

NaCMC employed in these investigations was purchased from Aldrich Chemical Company, Inc. The average molecular weight (M_w) of the sample was 90,000 with a degree of substitution

(DS) of 0.70 and these values agree well with those obtained from physiochemical characterization in the present study.

The alkali-metal salts (Fluka) were of purum or puriss grade; these were dried *in vacuo* for a prolonged period immediately before use and were used without further purification.

Conductance measurements were carried out on a Pye-Unicam PW 9509 conductivity meter at a frequency of 2000 Hz using a dip-type cell with a cell constant of 1.15 cm^{-1} and having an uncertainty of 0.01 percent. The cell was calibrated by the method of Lind and co-workers[4] using aqueous potassium chloride solution. The measurements were made in a water bath maintained within ± 0.005 K of the desired temperature. The details of the experimental procedure have been described earlier.[5,6] Several independent solutions were prepared and runs were performed to ensure the reproducibility of the results.

In order to avoid moisture pickup, all solutions were prepared in a dehumidified room with utmost care. In all cases, the experiments were performed at least in three replicates.

Results and Discussion

Primitive Additivity

Initially, we have analyzed the experimental specific conductivity data phenomenologically in terms of an additivity contributions of the polyelectrolyte and the simple salt to the total specific conductivity (known as 'primitive' additivity). Such an approach is usually used in the literature in describing the behaviour of salt-containing polyelectrolyte solutions.[7-10] Traditionally, this approach takes the form of an assumed additivity of the specific conductance of the polyelectrolyte and of the salt, which gives the specific conductance (κ) of the polyelectrolyte in a salt solution,

$$\kappa = \kappa_p + \kappa_S \tag{1}$$

where κ_p is the specific conductance of the polyelectrolyte in the absence of a simple salt and κ_s is the specific conductance of the simple salt in the absence of polyelectrolyte. In a polyelectrolyte-salt solution, therefore, the polyelectrolyte specific conductance is given by

$$\kappa_p = \kappa - \kappa_s \tag{2}$$

If a true additivity holds, the values of κ_p obtained for a given polyelectrolyte in salt-free (where $\kappa_s = 0$) and salt-containing solutions would be identical.

Figures 1-3 show the variation of the specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixtures containing respectively 10, 20 and 40 volume percent of acetonitrile in absence and in presence of NaCl. Figures 4-6 show the variation of the specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixtures containing 10 volume percent of acetonitrile in absence and in presence of KBr, KI and Na_2SO_4. Also included in these figures are the profiles following 'primitive' additivity and 'modified' additivity (discussed later).

It is clearly evident from Figures 1-6 that the 'primitive additivity' does not hold for the polyelectrolyte-salt systems investigated here.

The fact that the true value of the polyelectrolyte specific conductance cannot be calculated from the specific conductance data obtained in salt-containing polyelectrolyte solutions by using additivity of polyelectrolyte and simple salt specific conductances indicates clearly the existence polyelectrolyte-salt interactions. This kind of behaviour of polyelectrolyte-salt solutions has also been reported earlier for other systems.[7-10]

Modified Additivity

Later Ander group[7,8] modified the 'primitive' additivity by taking into account the Debye-Hückel interactions between the polyion and the salt ions to give the polyelectrolyte specific conductance in a polyelectrolyte-salt solution as

$$\kappa_P = \kappa - \kappa_S \left(D_2 / D_2^0 \right) \tag{3}$$

where D_2 and D_2^0 are the co-ion self-diffusion coefficients in a salt-containing polyelectrolyte solution and in an infinitely dilute polyelectrolyte-free salt solution, respectively. The ratio of self-diffusion coefficients D_2 / D_2^0 has been used as a quantitative measure of the effective interaction of uncondensed small ions in the presence of the polyelectrolyte, and hence the effective specific conductance of the added simple salt would be $\kappa_s \left(D_2 / D_2^0 \right)$.

Now, in absence of the experimental data for D_2 / D_2^0 for the present system, these were calculated by using the Manning's theory as[11]

$$D_2 / D_2^0 = 1 - (1/3)\xi X \left[2 + X \left(1 + \pi \xi^{-1} \right) \right]^{-1} \tag{4}$$

when $\xi < 1$, but when $\xi > 1$, D_2 / D_2^0 takes the following form

$$D_2 / D_2^0 = 1 - (1/3)\xi^{-1} X \left[\xi^{-1} X (1 + \pi) + 2 \right]^{-1} \tag{5}$$

Here X is the ratio of the equivalent polyelectrolyte concentration (c_p) to the equivalent salt concentration (c_s), and ξ is the charge density parameter of the polyelectrolyte.

Conclusions

Although the modified additivity is somewhat better than the primitive one, the departure is still prominent. Therefore, the effect of salts on the specific conductance is not described by the

additivity even if we take into account the interactions among all ionic species present in solution.

The observations indicate that

(1) the effective specific conductance of the added simple salt may not be given by $\kappa_s \left(D_2 / D_2^0 \right)$. The derivation of the salt diffusion ratio only takes into account the relaxation effect. The effect of electrophoretic countercurrent, which is neglected while deriving Eqs. (4) and (5), might play an important role,

(2) the polyion specific conductance is greatly affected by the addition of the salts. In the present case the polyion mobility should decrease with the addition of salts, suggesting the decrease in the apparent charge of the polyion due to its changing conformation in salt solutions,

(3) the contribution of the polyion to the specific conductance may be influenced by the solute-solvent solvodynamic interactions. Namely, the specific conductance depends on whether the polyion is free-draining or non-draining, and

(4) the polyion mobility is sensitive to the concentration of the added salt which might induce some conformational changes in the polyion structure thus affecting its specific conductance in salt solutions. The effect is found to be more prominent as the concentration of the added salt is increased.

References

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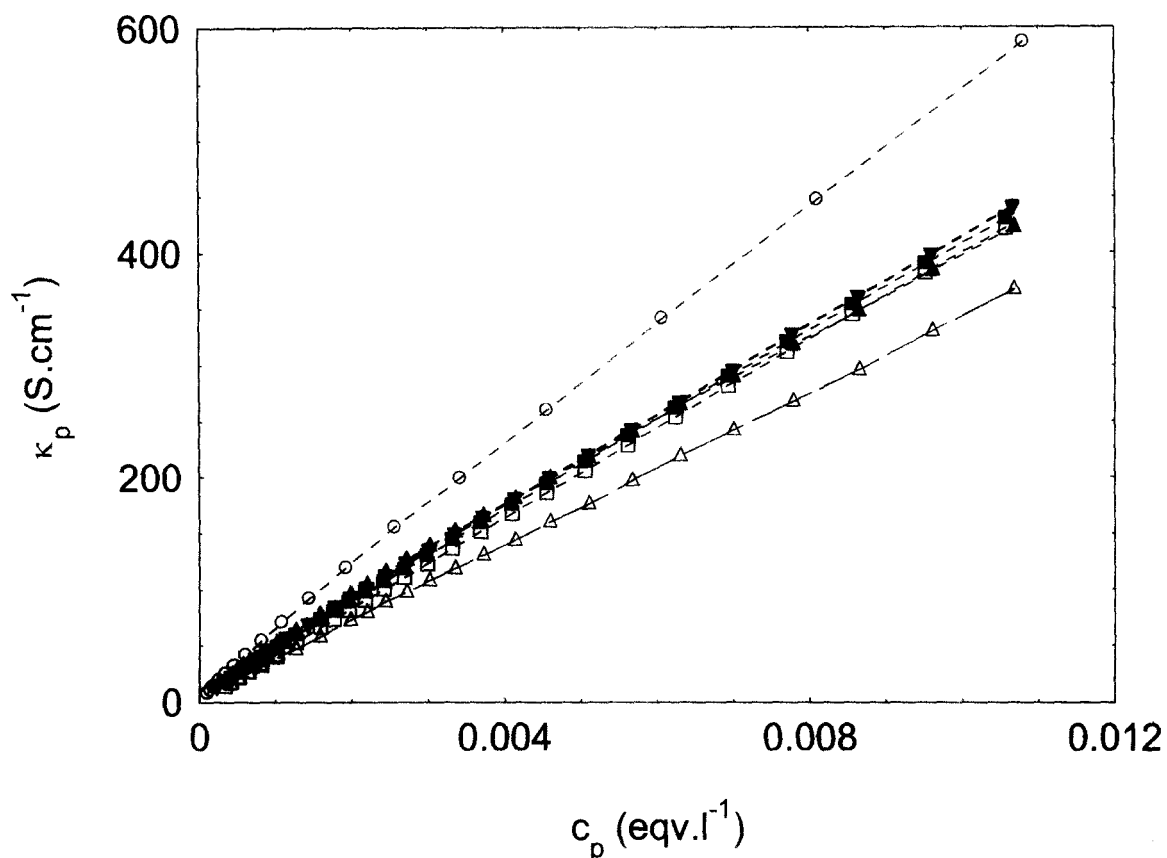
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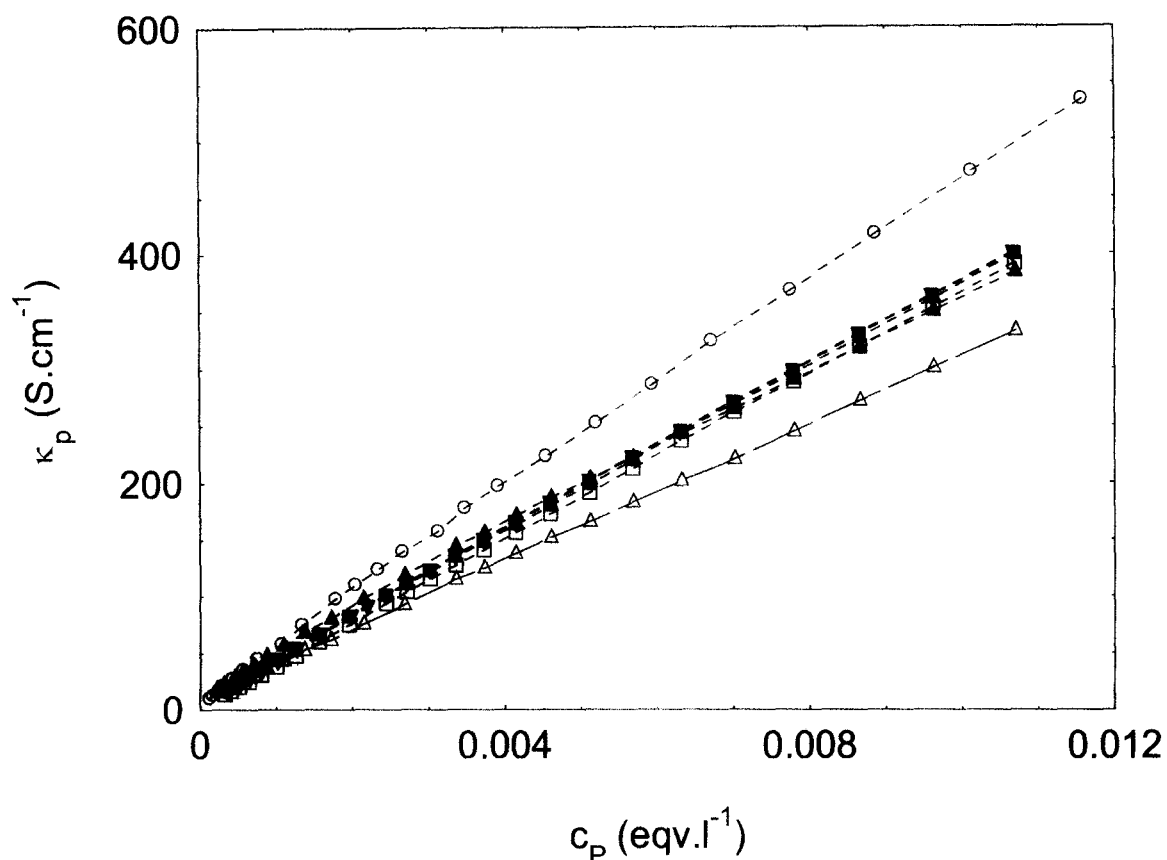
Figure 1. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 10 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares and up triangles represent the polyelectrolyte solutions in presence of 0.0001, 0.001 and 0.01 eqv.l^{-1} NaCl respectively.
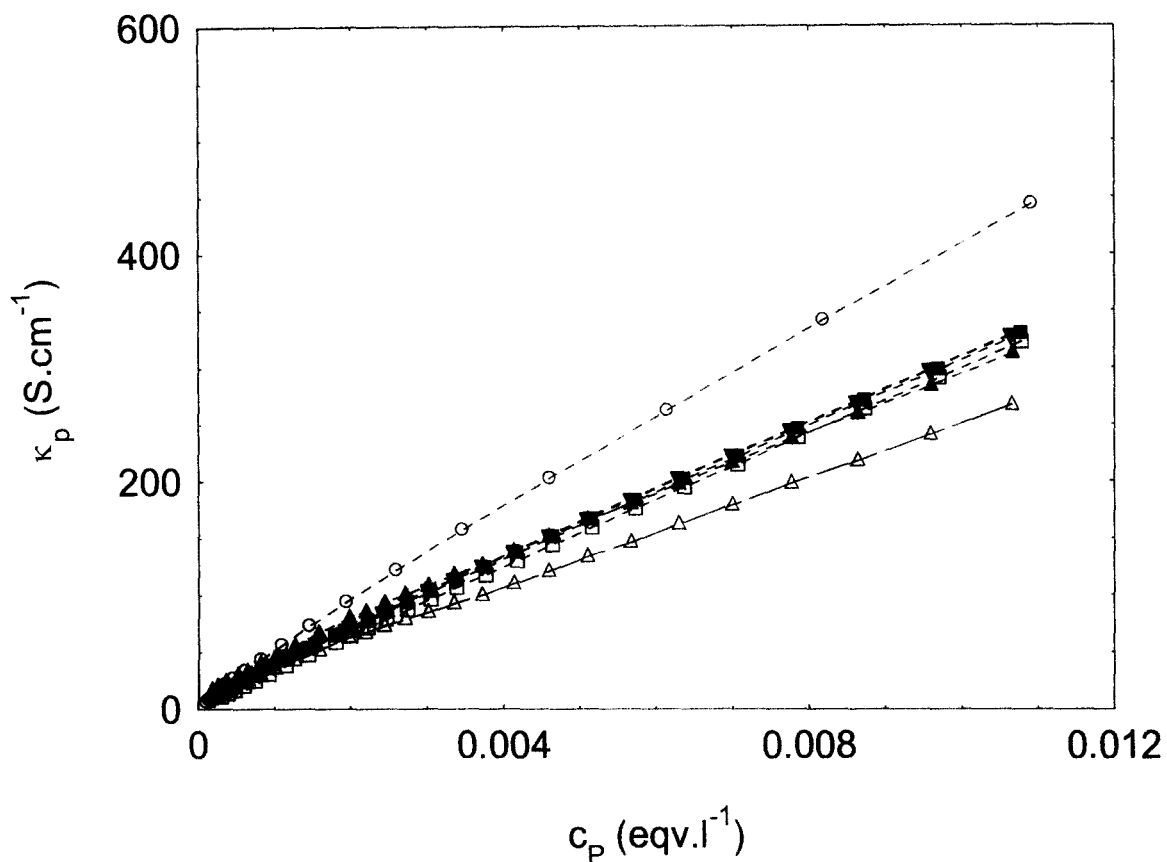
Figure 2. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 20 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares and up triangles represent the polyelectrolyte solutions in presence of 0.0001, 0.001 and 0.01 eqv.l^{-1} NaCl respectively.
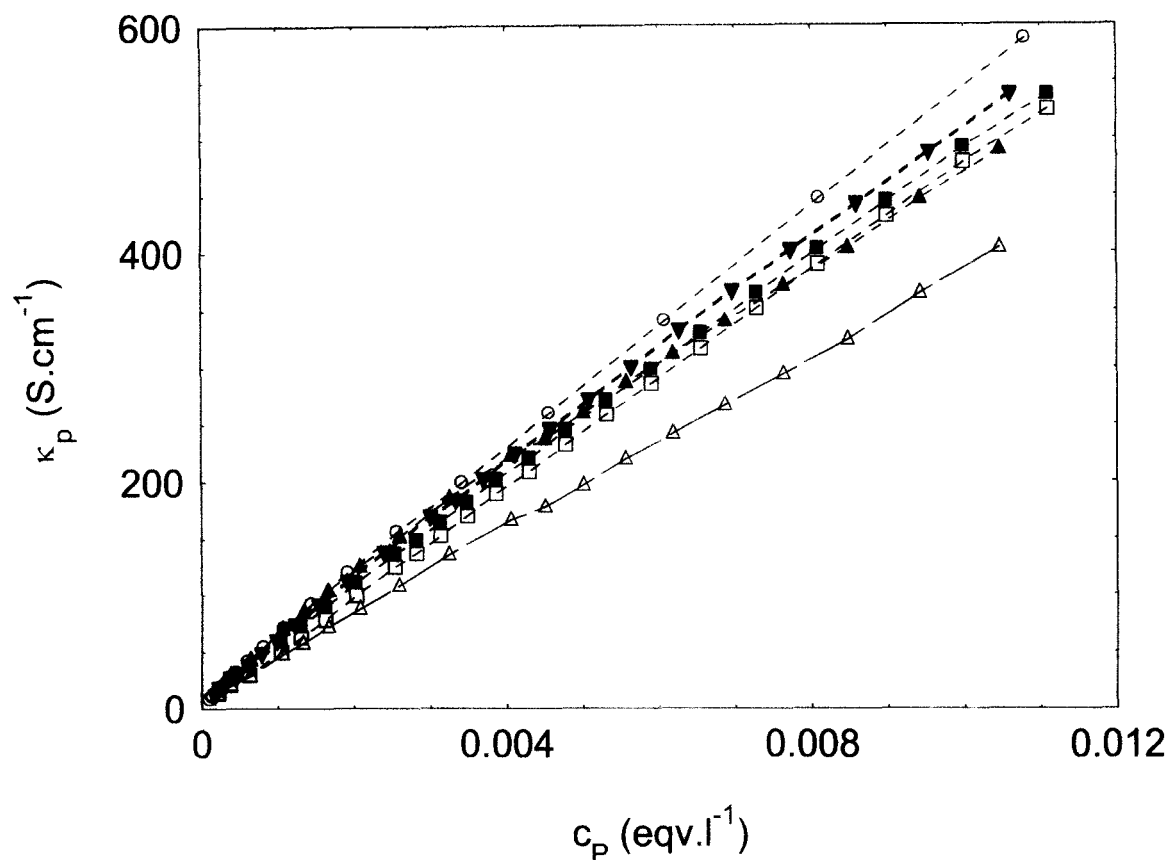
Figure 3. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 40 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares and up triangles represent the polyelectrolyte solutions in presence of 0.0001, 0.001 and 0.01 eqv.l^{-1} NaCl respectively.

Figure 4. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 10 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares and up triangles represent the polyelectrolyte solutions in presence of 0.0001, 0.001 and 0.01 eqv.l^{-1} KBr respectively.
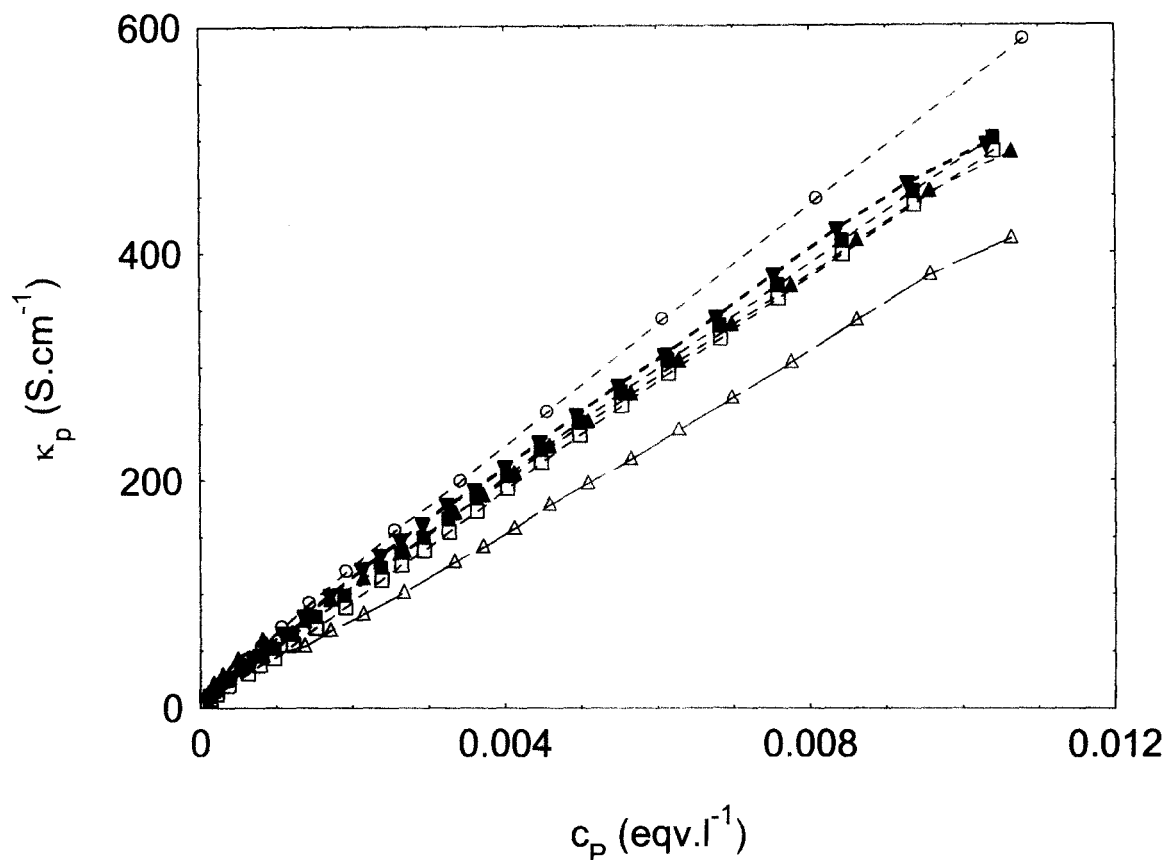
Figure 5. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 10 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares and up triangles represent the polyelectrolyte solutions in presence of 0.0001, 0.001 and 0.01 eqv.l^{-1} KI respectively.
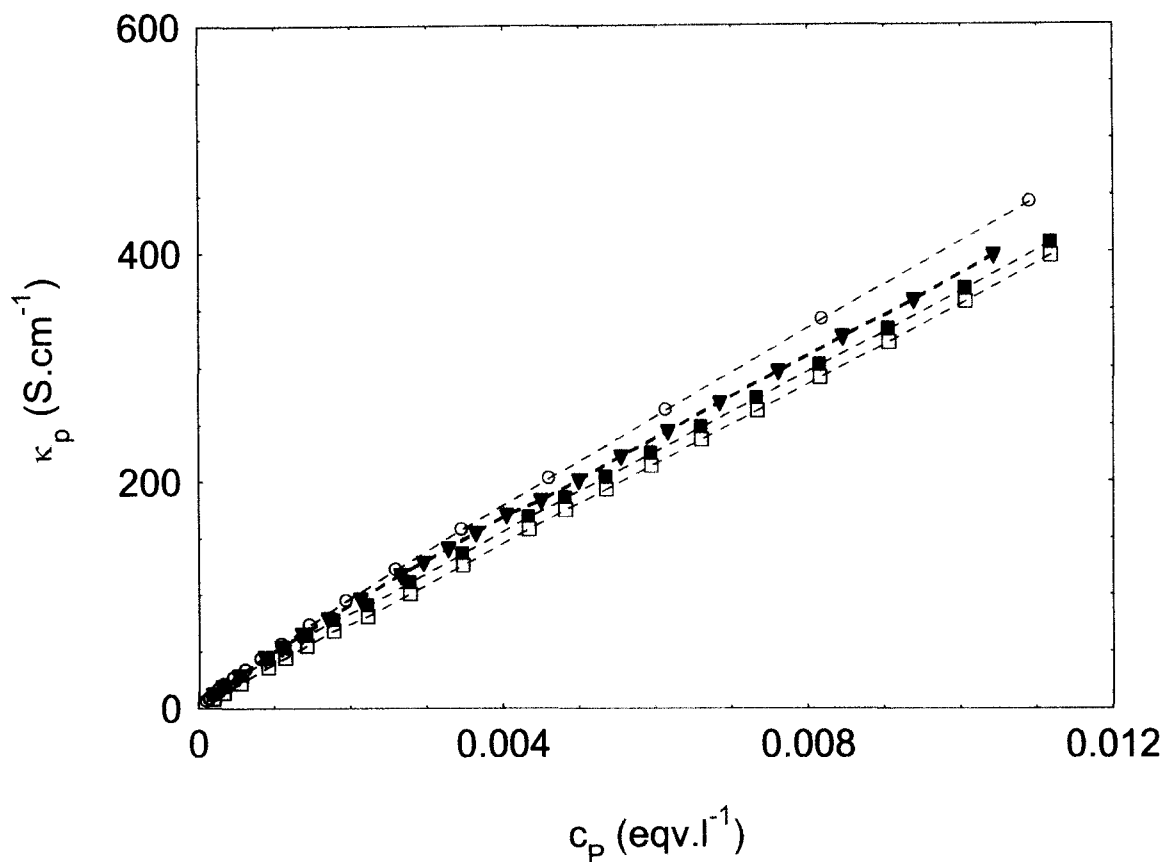
Figure 6. Specific conductivities of NaCMC as a function of the polymer concentration (c_p) at 308.15 K in acetonitrile-water mixture containing 10 volume percent acetonitrile: Circles, salt-free solution; Open symbols represent primitive additivity whereas the closed symbols represent modified additivity. Down triangles, squares represent the polyelectrolyte solutions in presence of 0.0001 and 0.001 eqv.l^{-1} Na$_2$SO$_4$ respectively.