

Electrical Conductivity of Poly(acrylic acid) – Polyacrylamide Complexes

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ABSTRACT: The conduction mechanism in the interpolymer complex resulting from the interaction between poly(acrylic acid) (PAA) and polyacrylamide (PAAm) was investigated. The characteristic features of the relation between the logarithm of conductivity, $\log \sigma$, and $1/T$ are different from those corresponding to the individual components of the complex. The value of σ for the complex was found to be less than its corresponding values for PAA or PAAm. The effects of the weight fraction of each polymer and the ionic strength of the solutions on the conductivity of the complex were also studied. The data showed that the σ of the complex depends on the weight fraction of the polymers. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 2049–2055, 1998

Key words: poly(acrylic acid); polyacrylamide; interpolymer complexation; infrared spectra; electrical conductivity

INTRODUCTION

The structure and stability of the poly(acrylic acid)–polyacrylamide (PAA–PAAm) complex have been studied in recent years using fluorescence spectroscopy, viscosity, and FTIR spectroscopy.^{1–6} Although a number of authors have studied the electrical conductivity of PAA and PAAm, the conductivity of the interpolymer complexes resulting from the interaction between the two polymers has not yet been investigated. Narasimha Rao and Subba⁷ studied thermally stimulated discharge currents in PAAm as a function of the polarizing field strength and concluded that the Poole–Frenkel model describes the dominant mechanism. Blythe⁸ stated that polyamides show pronounced ionic conduction effects at elevated temperatures, evidently as a result of the dissociation of amide groups to give protons. The aim of

the present work was to study the conduction mechanism in the interpolymer complex between PAA and PAAm.

EXPERIMENTAL

Polyacrylamide (PAAm; $\text{CH}_2\text{CHCONH}_2$) was obtained from BDH Chemicals, Pool, England; its molecular weight is over 5,000,000. Poly(acrylic acid) (PAA; CH_2CHCOOH ; PW-110, Lot No. 4029), in the form of a white powder, was obtained from Nisso SHOJI Co., Japan. The two polymers (in the form of white powders) were used as obtained from the manufacturers without any further purification. A solution of each polymer was prepared by dissolving 1 g/100 mL of distilled water. Each solution was then stirred overnight to ensure complete dissolution. Mixtures from the two polymer solutions with different PAA weight fractions, W_{PAA} , were prepared and thin films were cast onto polyethylene dishes and dried at room temperature for several days.

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Also, solutions of PAA were prepared in electrolytes of NaCl with various ionic strengths (IS), namely 0, 0.001, 0.005, and 0.02M, and mixtures of the two polymer solutions were prepared. The pH of these mixtures was then adjusted by the drop addition of 10% HCl until precipitation or phase separation took place. The precipitate was filtrated and washed with distilled water to remove any soluble salts. The samples were dried in an oven at 90°C for 6 h. Samples prepared for the purpose of electrical measurements are in the form of either thin films or compressed discs. In the case of mixtures between PAA and PAAm, we deal with films, whereas in case of the precipitates, we deal with compressed discs. The samples taken from thin films were of thickness in the range 20–30 μm , depending on the composition of the mixture film. For discs, 150 mg of the powdered sample (average particle size $\approx 100 \mu\text{m}$) was pressed in a special die under a vacuum hydraulic (6 tons) to give a disc of 13 mm diameter and ≈ 0.9 –1.0 mm thickness, depending on the nature of the powder.

Electrodes were made on each sample by painting with a silver-conducting paste. The samples were then desiccated for 24 h before electrical measurements. The temperature of the sample was changed by heating it in a shielded electric heater, connected to a variac which gives linear changes in temperature.

The I–V characteristics of the samples were measured at voltages up to 400 V, in the case of discs, and to 150 V, in the case of films. The electric conductivity of the samples was determined as a function of temperature with a rate of heating of 1.5°C/min and under a dc voltage of 150 V, in the case of discs, and 10 V, in the case of films. Voltage was applied to the samples using a HEATHKIT regulated H.V. power supply Model IP-17 (range: 0–400 V). The current passing through the samples was measured with a Keithley 616 electrometer. The operating temperature range was 30–130°C, where the higher temperature is limited by the degradation and deformation of the PAA samples. Electrical measurements were carried out in duplicate and the mean value was taken and the error was $\pm 1\%$.

RESULTS AND DISCUSSION

The relation between $\log \sigma$ versus $1/T$ is drawn in Figure 1. This relation is linear over the entire temperature range and the apparent activation

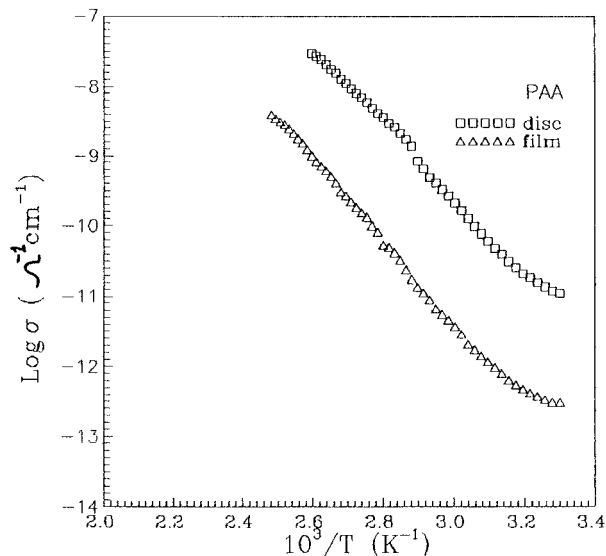


Figure 1 Temperature dependence of log dc conductivity of PAA.

energy of conduction was evaluated from the equation

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{KT}\right) \quad (1)$$

where σ is the conductivity at temperature T ; σ_0 , the conductivity at very high temperature; E_a , the apparent thermal activation energy of conduction; and K , Boltzmann's constant. From this relation, E_a was found to be 1.14 eV.

To investigate the appropriate conduction mechanism taking place in this sample, the I–V characteristics were also plotted at different constant temperatures. It was found that the I–V characteristics up to 200 V are ohmic in nature at all studied temperatures.

The log current versus square root of electric field, $E^{1/2}$, at different temperatures is represented graphically in Figure 2. It is clear from this relation that the current verifies the relation

$$I \propto \exp(e\beta E^{1/2}/KT) \quad (2)$$

where β is a coefficient to be estimated and I , $E^{1/2}$, and K have their above definitions. This relation implies that at high electric fields $\log I$ changes linearly with $E^{1/2}$, whereas at low fields ($E^{1/2} < 125 \text{ V cm}^{-1}$), this relation deviates from linearity, probably due to the accumulation of space charges at the electrodes.⁹

To determine the actual conduction mechanism

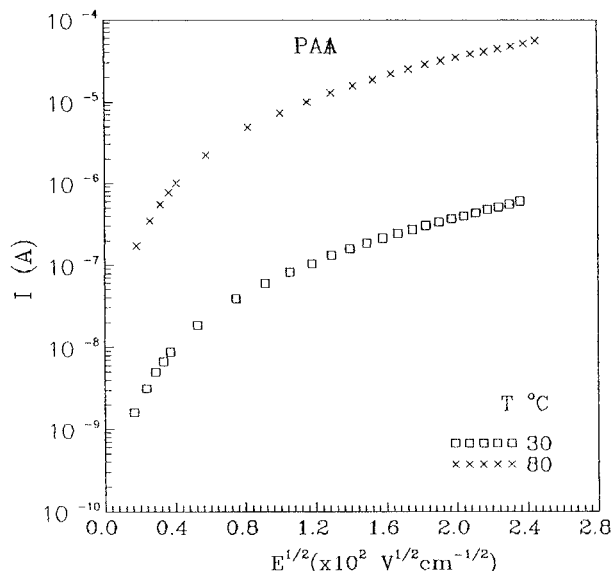


Figure 2 $I-E^{1/2}$ characteristics of PAA at different temperatures.

at different temperatures, the values of β , deduced from the slope of plots of I versus $E^{1/2}$, are compared with theoretical values in Table I. The calculated values of β were estimated from the relation

$$\beta_{PF} = 2(e/4\pi\epsilon\epsilon_0)^{1/2} \tag{3}$$

where ϵ is the dielectric constant of PAA (the measured value of ϵ of small differences between experimental and theoretical values may be the result of the presence of impurity centers and/or the heterogeneity of the electric field in the sample⁹).

At low temperature, normal conduction may take place due to hopping¹⁰ between localized states. In this case, the temperature dependence of the conductivity may be decreased:

$$\log \sigma = A - BT^{-1/4} \tag{4}$$

where A and B are constants. Based on that, it could be pointed out that the hopping process be-

Table I Experimental and Calculated Values of β at Different Temperatures for PAA Film

T (°C)	$10^5 \beta_{exp}$	$10^5 \beta_{PF}$
27	3.51	
50	—	3.61
80	3.88	

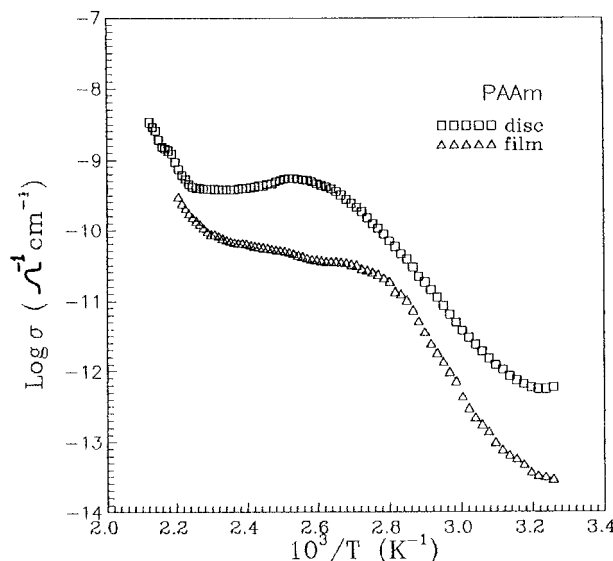


Figure 3 Temperature dependence of log dc conductivity of PAAm.

tween localized states with the potential barrier being lowered by the applied field, according to the Poole–Frenkel type, may be the dominant mechanism over the entire temperature range.

Figure 3 represents the variation of the electrical conductivity of the annealed PAAm as a function of $1/T$, using the same relations mentioned above. The characteristic features of the curve are an initial sharp increase of σ up to 87°C, followed by a moderate increase up to 140°C, then by a final rapid increase up to 180°C. The determined values of the activation energies of the samples are 1.7, 0.4, and 0.78 eV for the high, medium, and low regions of temperature, respectively. The $I-V$ characteristics of PAAm were also examined. It was found that at any temperature the $I-V$ relations are ohmic.

Currents are plotted against $E^{1/2}$ at different temperatures in Figure 4. For all of these, I varies linearly with $E^{1/2}$ at higher fields but exhibits an appreciable deviation from linearity at lower fields ($E^{1/2} < 160 \text{ V cm}^{-1}$). Accordingly, the conduction mechanism may be attributed to the Poole–Frenkel effect where charge carriers can be released due to the ionization of impurity centers in the sample. The values of β were calculated and are given in Table II together with the theoretical value for comparison.

It is apparent from the table that the experimental values of β are comparable with the theoretical values of the Poole–Frenkel coefficient β_{PF} . On the basis of the above-mentioned consid-

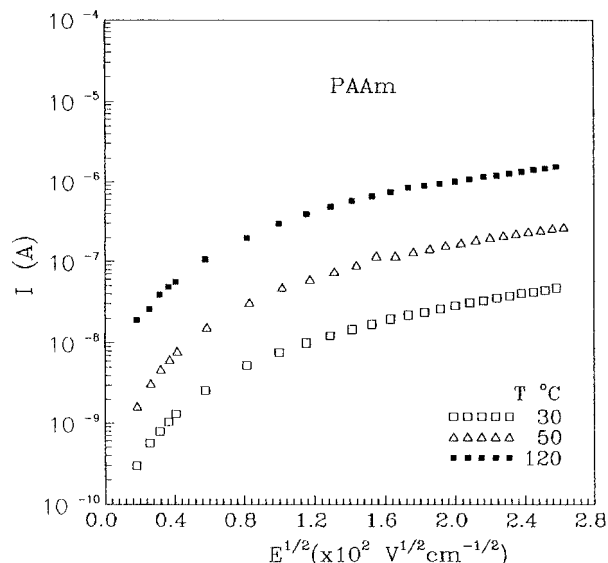


Figure 4 $I-E^{1/2}$ characteristics of PAAm at different temperatures.

erations, it could be concluded that the conduction mechanism in the temperature range 85–140°C may be either electronic or ionic where amide groups would dissociate, giving up protons.

The variation of $\log \sigma$ versus $1/T$ for films of PAA–PAAm mixtures with different W_{PAA} , from 0 to 1, is shown in Figure 5. The characteristic features of the curves corresponding to the mixtures having a W_{PAA} lower than 0.4 are more or less similar to those of the curve of pure PAAm. As W_{PAA} is increased, these features approach gradually those of the curve of pure PAA.

The activation energies in these films were evaluated in the temperature range (27–80°C) and are given in Figure 6 together with the values calculated from the empirical equation

$$E_{a\text{cal}} = E_{a1}W_{PAA} + E_{a2}(1 - W_{PAA}) \quad (5)$$

where $E_{a\text{cal}}$ is the calculated value of the mixture and E_{a1} and E_{a2} are the measured values of PAA and PAAm, respectively.

It is obvious from this relation that as W_{PAA} is

Table II Experimental and Calculated Values of β at Different Temperatures for PAAm Film

T (°C)	$10^5 \beta_{\text{exp}}$	$10^5 \beta_{\text{PF}}$
27	2.50	
50	2.40	2.41
80	2.54	

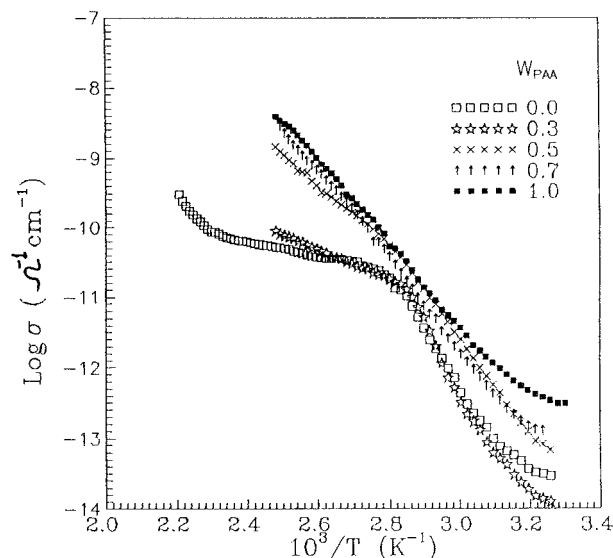


Figure 5 Temperature dependence of \log dc conductivity of films of PAA–PAAm mixtures.

increased the activation energy decreases. It is also apparent that the experimental values are in good agreement with the calculated ones. It could be mentioned that the linear behavior of E_a with W_{PAA} provides strong evidence that there is no interaction between PAA and PAAm in their mixtures.

To determine the conduction mechanism taking place in these films, the $I-V$ characteristics were studied at different constant temperatures. It was found that these characteristics are also ohmic in nature.

Figure 7 represents the relation between I and $E^{1/2}$ at different values of temperature. It is evident from these figures that I varies with $E^{1/2}$ in a manner analogous to that for PAA and PAAm

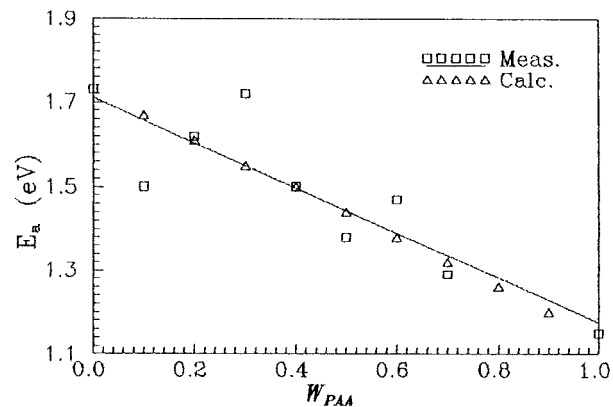


Figure 6 Variation of the activation energy of conduction, E_a , of the PAA–PAAm mixtures with W_{PAA} .

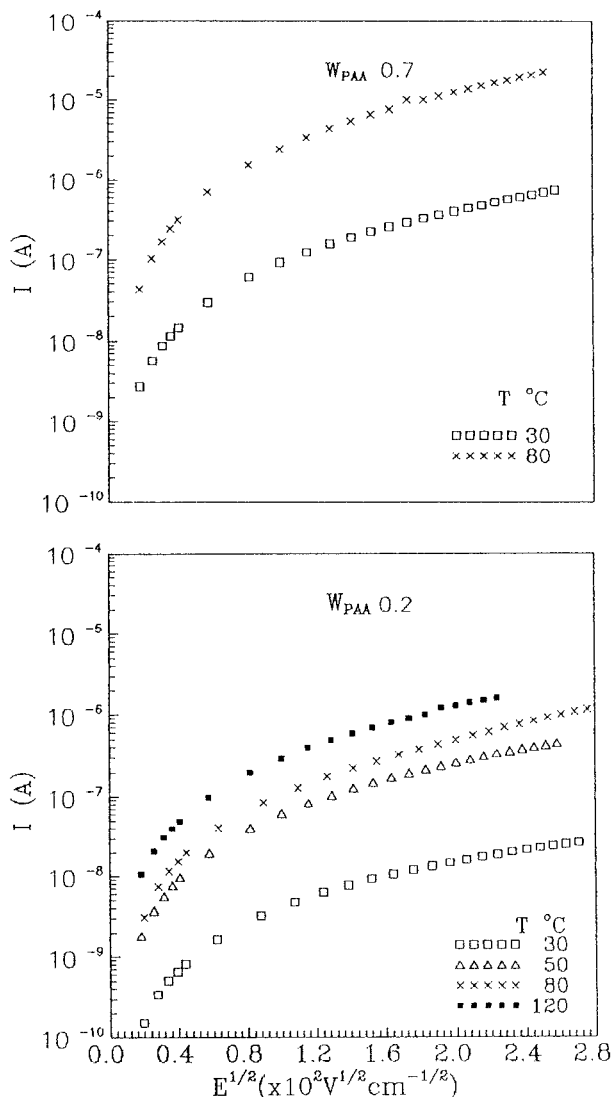


Figure 7 $I-E^{1/2}$ characteristics of films of PAA-PAAM mixtures of different W_{PAA} at different temperatures.

films. The values of β were evaluated and are compared with the theoretical values of β_{PF} in Table III. It is evident that the Poole-Frenkel mechanism is still operating from data generated on these films.

The precipitate formed as a result of interpolymer complexation between PAA and PAAM, $W_{PAA}^{0.5}$, was prepared for electrical measurements in the form of a compressed disc of thickness 1 mm. Figure 8 illustrates the variation of the electrical conductivity of the complex as a function of $1/T$, together with those of the individual components. The complex has characteristic features which are completely different from those of the individual components. The values of the conduc-

Table III Experimental and Calculated Values of β at Different Temperatures for the Film PAA-PAAM Mixtures

W_{PAA}	$10^5 \beta_{PF}$	$10^5 \beta_{exp}$			
		27°C	50°C	80°C	100°C
0	2.40	2.50	2.40	—	2.54
0.1	—	2.59	2.14	2.77	—
0.2	2.82	2.21	2.78	3.73	4.15
0.3	2.73	2.54	3.47	3.98	5.30
0.4	2.85	2.86	2.54	3.45	3.89
0.5	2.87	2.98	2.94	2.86	—
0.6	3.08	2.85	—	3.98	—
0.7	2.94	2.85	—	3.43	—
1.0	3.61	3.51	—	3.88	—

tivity of the complex are below those of PAA and PAAM. This may be due to the decrease in mobility as a result of the interaction between the polymers and, hence, the conductivity becomes lower than that of the individual polymers. The conductivity increases linearly with increasing temperature up to 130°C, but the rate of increase is different in different temperature regions: It is rapid at low temperatures ($T < 96^\circ\text{C}$), slow at moderate temperatures ($96 < T < 122^\circ\text{C}$), and considerably faster up to 130°C. Oyama et al. reported that the addition of PAA¹¹ or poly(methacrylic acid) (PMAA)¹² to poly(ethylene glycol) (PEG) induces a decrease of the intermolecular mobility of the

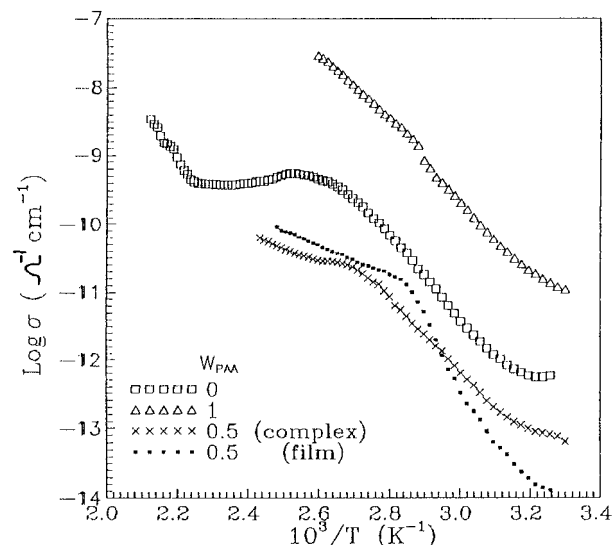


Figure 8 Temperature dependence of log dc conductivity of PAA-PAAM complex compared with those of PAA, PAAM, and their mixture films.

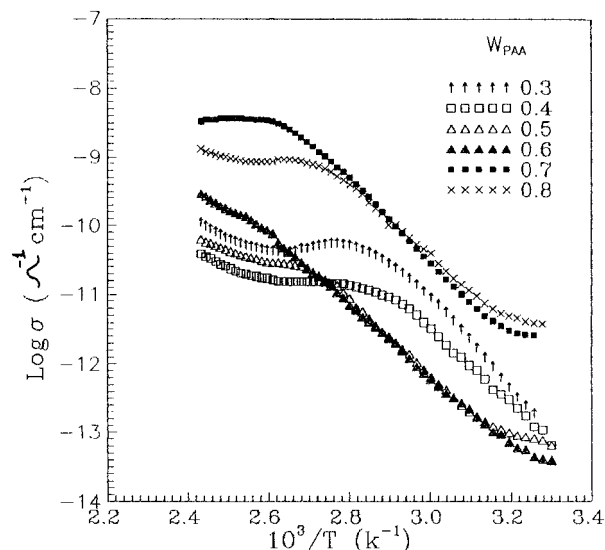


Figure 9 Temperature dependence of log dc conductivity of the PAA-PAAM complexes with different W_{PAA} .

PEG chains as a result of complexation using fluorescence spectroscopy. The activation energies in the three temperature regions are 0.48, 0.27, and 1.1 eV, respectively. Complexes from the two polymers, containing different values of W_{PAA} (0.3–0.8), were prepared, as mentioned in the Experimental section, and processed in the form of discs. The conductivities in these complexes are shown in Figure 9. The activation energies were evaluated in the first linear temperature region and are plotted against W_{PAA} in Figure 10 together with the values calculated using eq. (5). It appears from this relation that the activation energies assume more or less equal values over the W_{PAA} range of 0.4–0.6, whereas they exhibit higher values for W_{PAA} below or above this range. Also, this

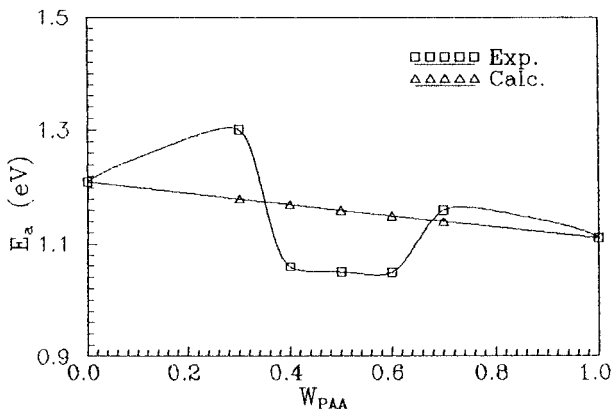


Figure 10 Variation of the activation energy, E_a , of the PAA-PAAM complexes with W_{PAA} .

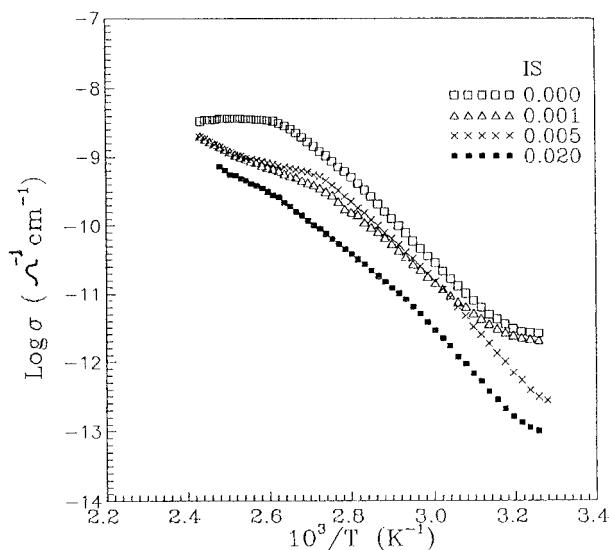


Figure 11 Temperature dependence of log dc conductivity of the PAA-PAAM complexes at different IS with W_{PAA} 0.7.

relation signifies that these samples are interpolymer complexes and not mixtures (as shown by the linear curve) from the two polymers.

From this figure, one can conclude that the structure of the complexes containing W_{PAA} in the range of 0.4–0.6 is the same, which anticipates that the complexation between PAA and PAAM is stable in this range. This may be because the molecular weights of the monomers of PAA and PAAM are nearly equal (≈ 72 g/mol) and, therefore, all units interact with each other when the ratios of the polymers are close. When W_{PAA} is beyond that range, the complexes may contain some residues of the noninteracting polymers and, therefore, the extreme PAA-PAAM complexes are produced.

The effect of the ionic strength (IS) of the PAA-PAAM solution on the PAA-PAAM complex precipitates was also investigated. The relationship between the log σ and $1/T$ of complexes with different IS and W_{PAA} was studied. As an example of this study, Figure 11 represents this relation for $W_{PAA}^{0.7}$.

Table IV shows the variation of the conductivity of the complexes with IS for W_{PAA} 0.7 in two different temperature regions, below and above 100°C. The conductivity of the complexes decreases, in general, as IS increases from 0 to 0.02M NaCl. This result can be explained on the basis that the IS increases the complexation which restricts the mobility of chains. Therefore,

the conductivity of the PAA–PAAm complexes decreases.

The activation energies of conduction in these complexes in the temperature region (27–100°C) are given in Table V. From this table, one can observe that the changes in the activation energies with IS are relatively small, indicating that the mechanism of conduction in these complexes are nearly similar irrespective of the ionic strength of the solution.

CONCLUSIONS

The foregoing data and its interpretation demonstrate that the Poole–Frenkel mechanism of conduction, namely, the field-assisted thermal ionization of traps, is dominant in the films of PAA and PAAm at high temperature, whereas hopping between the localized states with decrease of the potential barrier due to the applied field may be dominant at low temperatures. The lower values of conductivity of the complex than those of PAA and PAAm was attributed to the fact that when the two polymers interact the mobility of the polymer chains decreases and, hence, the conductivity decreases. The activation energy of conduction in the complex depends on the weight fraction, W_{PAA} , of each polymer in the complex. The activation

Table IV Variation of the Conductivity with the Ionic Strength (IS) in the PAA–PAAm Complexes of W_{PAA} 0.7

IS (<i>M</i> NaCl)	σ ($\times 10^{-10} \Omega^{-1} \text{cm}^{-1}$)	
	80°C	120°C
0	3.23	35.60
0.001	1.09	9.17
0.005	1.50	9.45
0.020	0.28	1.50

Table V Variation of the Activation Energy with Ionic Strength for W_{PAA} 0.7 Complexes

IS (<i>M</i> NaCl)	E_a (eV)
0	1.16
0.001	1.05
0.005	1.24
0.020	1.12

energy assumes more or less constant values over the range of W_{PAA} from 0.4 to 0.6, which means that the complex is stable in this range. The conductivity of the complex decreases as the IS of the solution increases.

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