

Infrared Spectroscopy and Electrical Properties of Ternary Poly(acrylic acid)–Metal–Poly(acrylamide) Complexes

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ABSTRACT: Fourier transform infrared spectroscopy (FTIR) and electrical measurements were used for the characterization of the interpolymer complexation between poly(acrylic acid) (PAA) and poly(acrylamide) (PAAm) and also the ternary PAA–metal–PAAm complexes. The interpolymer complexes were prepared by adjusting the pH value of the mixture solutions at different PAA weight fractions (W_{PAA}). The ternary complexes were prepared by mixing metal chloride solutions (such as ErCl_3 and LaCl_3) with different concentrations to PAA–PAAm mixtures and adjusting the pH value for different W_{PAA} . It was found that the IR spectra of the interpolymer complexes showed absorption bands at shifted positions and of intensities different from those of the parent polymers. Also, the examination of the spectra of the ternary metal–polymer complexes revealed that they depend on the nature, valency, ionic radius, and concentration of the added metal chlorides. Analysis of the electrical results showed that the electrical conductivity of the interpolymer complexes are always lower than those of PAA and PAAm, which was attributed to the decrease in the mobility of the polymer chains as a result of the complexation. Also, the conductivity of the ternary metal complexes showed a dependence on the properties of the additives and were found to decrease with increasing their concentrations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2699–2705, 2002

Key words: FTIR; ternary metal complexes; conducting polymers; water-soluble polymers; interpolymer complexes

INTRODUCTION

The combination of materials with different physical and/or chemical nature, such as metals and polymers, seems to be a relatively unexplored area of research that offers great possibilities for developing novel materials.

Interpolymer interactions between synthetic water-soluble polymers have been a subject of investigation for several researchers. These complexes possess various unique properties that are different from those of the individual compo-

nents.^{1–3} They can be used in dialysis, ultrafiltration, reverse osmosis, blood-compatible materials, and batteries.³

It is believed^{3,4} that when two chemically different macromolecules approach each other, the molecular interaction energy is affected by several types of secondary binding forces, coulomb hydrogen bonding, van der Waals forces, charge transfer, and hydrophobic interactions. The formation of the complex has been investigated by several techniques such as viscometry,^{1,4–7} turbidimetry,⁵ fluorescence,^{3,4,8–16} conductometry, potentiometry,^{5,7,17} and light-scattering measurements. However, only a few studies have been carried out on the polymer complexes in the solid state. FTIR and differential scanning calorimetry

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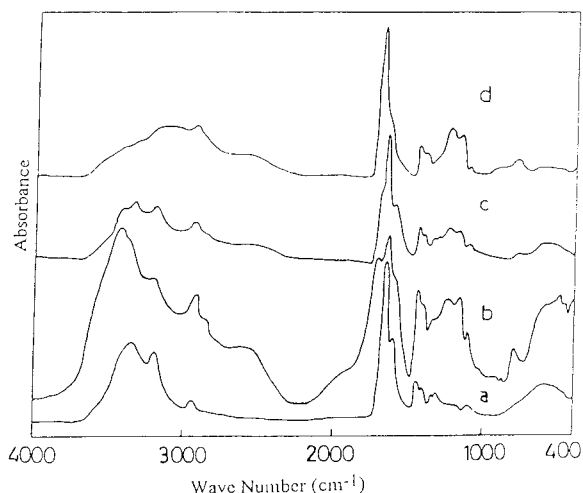


Figure 1 FTIR spectra of (a) pure PAAm, (b) PAA-PAAm complex, (c) PAA-PAAm mixture film, and (d) pure PAA film.

analyses are now used in examination of the complex system in the solid state.^{18,19}

Studies have been started recently of polymer-metal systems incorporating two polyelectrolytes of opposite charges and metal ions. This trend is based on the chemistry of intermacromolecular reactions and coordination chemistry of polymer-metal compounds. Fairly detailed studies have been carried out on the formation, structure, and properties of ternary metal-polymer complexes (TMPC).^{20,21}

In a number of instances the necessity arises of imparting electrical conductivity to a polymer, while preserving its inherent complex of properties. To prove this new property, it is necessary to

alter the chemical structure of the polymer such that its molecules should consist of an alternating sequence of double or triple bonds, or it should form charge-transfer complexes. The desired result can also be achieved by introducing metal atoms into the composition of the macromolecules.

EXPERIMENTAL

The polymers used in this work are (1) poly(acrylamide) [PAAm; obtained from BDH Chemicals (Poole, UK); molecular weight > 5,000,000 g/mol] and (2) poly(acrylic acid) [PAA; obtained from Nisso Shoji Co. (Japan) (PW-110, lot no. 4029)]. The two polymers (in the form of white powders) were used as obtained from the manufacturers without any further purification.

A stock solution from each polymer was prepared by dissolving each polymer in distilled water in the concentration 1 g/100 mL and 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 by mixing the two stock solutions in the appropriate proportions.

$$W_{\text{PAA}} = \frac{W(\text{PAA})}{W(\text{PAA}) + W(\text{PAAm})} \quad (1)$$

where $W(\text{PAA})$ and $W(\text{PAAm})$ are the weight of PAA and PAAm in g, respectively, such that the total polymer concentration in each mixture is kept constant. These mixtures were stirred over-

Table I Frequencies of the Absorption Bands of Samples and Their Assignments

PAAm	Mixture	Complex	PAA	Assignment
	3413	3441	3000–3450	$\nu(\text{O—H})$
3350				$\nu(\text{N—H})$
3213	3202	3216		$\nu(\text{N—H})$
2936	2940	2927	2955	$\nu(\text{C—H})$
	1713		1718	$\nu(\text{C=O})$ acid
1670	1663	1648		$\nu(\text{C=O})$ amide
1616	1608	1583		(N—H)
1454	1451	1443	1456	(C—H)
1420		1410	1415	$\nu(\text{C—O})$
1350				$\nu(\text{C—H}), \nu(\text{C—N})$
1324				$\nu(\text{C—H}), \nu(\text{C—N})$
1123	1250	1238	1248	Skeletal vibration
	1173	1168	1174	(O—H), $\nu(\text{C—O})$

night, after which thin films were prepared by casting a definite volume of each mixture onto polyethylene dishes, followed by drying in air for about 3 days. The peeled films were then dried in an oven at 90°C for about 6 h. The pH of some mixtures was adjusted by adding drops of 10% HCl until precipitation or phase separation took place.³ The precipitates were filtrated and washed with distilled water. The samples were then ground in an agate mortar followed by sieving to a particle size of 100–120 μm suitable for IR and electrical measurements. Other mixtures from the two polymers of W_{PAA} of 0.3, 0.5, and 0.7 were treated by aqueous solutions of ErCl_3 , LaCl_3 , CeCl_3 , and SrCl_2 . The concentrations of these chlorides are 5, 10, and 20 wt % from the total weight of polymers in each mixture, dissolved in 10 mL distilled water. These aqueous solutions were added to the polymer mixtures and stirred. Infrared spectra were recorded on a Perkin-Elmer 1650 FTIR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT) using the KBr technique in the case of precipitates. Samples prepared for the purpose of electrical measurements were in the form of either thin films or compressed discs (in the case of precipitates). Electrodes were made on each sample by painting silver-conducting paste. The electric conductivity of the samples was determined as a function of temperature with 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. The current passing through the samples was measured with a Keithley 616 electrometer (Keithley Metrabyte, Taunton, MA). The conductivity of the samples was determined from the relation

$$\sigma = \frac{IL}{AV} \quad (2)$$

where σ is the electrical conductivity ($\Omega^{-1} \text{cm}^{-1}$), I is the current passing through the sample (A), L is the thickness of the sample, V is the voltage applied to the sample (V), and A is the cross-sectional area of the sample (cm^2).

RESULTS AND DISCUSSION

The FTIR spectra of PAAm, PAA, and their W_{PAA} 0.5 mixture and complex are shown in Figure 1. The frequencies of the absorption bands of these samples together with their assignments are given in Table I. Examination of the spectra and

table reveals that the mixtures displays absorption bands at frequencies that represent the characteristic absorption bands of the individual components of the mixture. On the other hand, it is clear that the spectrum of the precipitate (interpolymer complex) shows similar spectral features, although the bands appear at shifted positions and with different intensities. These differences in positions and intensities of the absorption bands are attributed to the formation of the interpolymer complex resulting from the interaction between PAA and PAAm solutions at

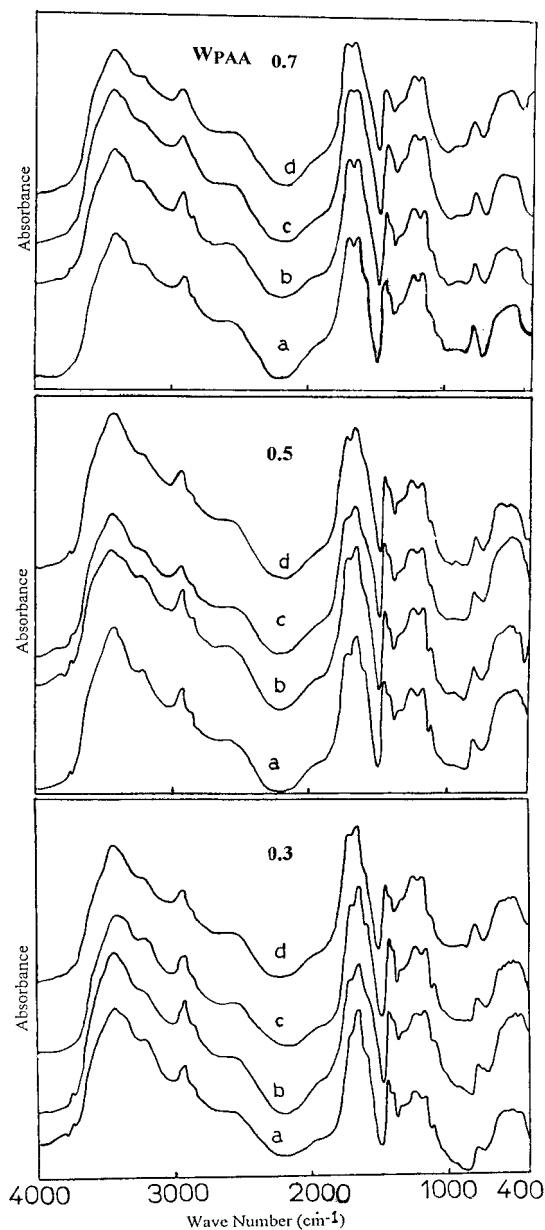


Figure 2 FTIR spectra of the ternary PAA- Er^{3+} -PAAm complexes with various ErCl_3 concentrations.

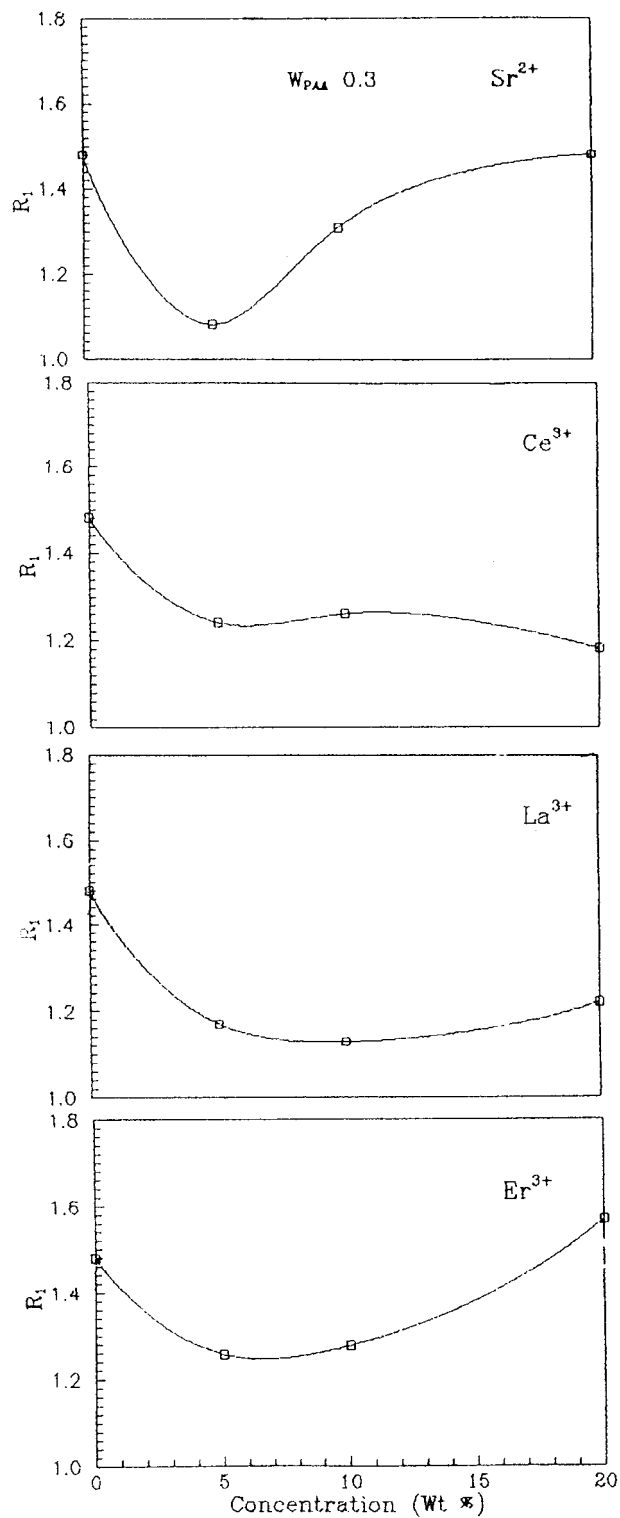


Figure 3 Variation of the absorbances ratio R_1 with the concentrations of metal cations in the PAA-PAAM-metal complexes of $W_{PAA} 0.3$.

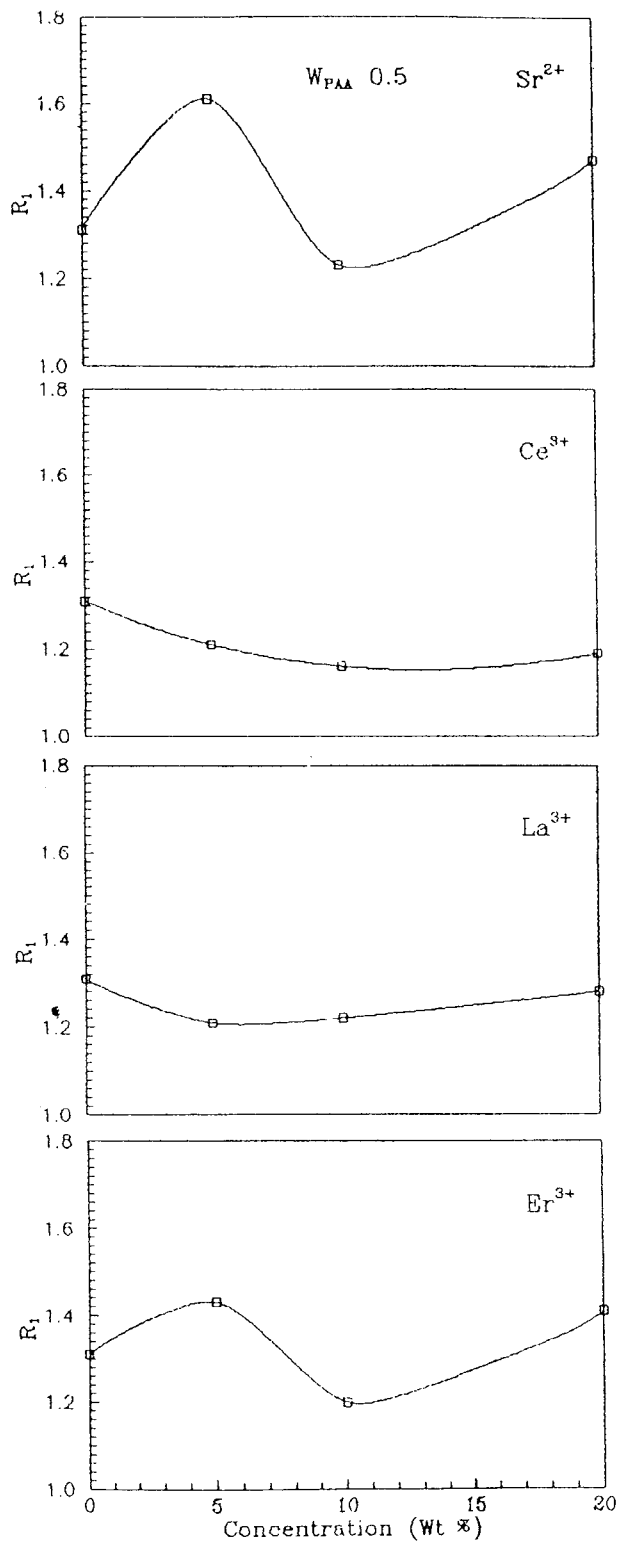


Figure 4 Variation of the absorbances ratio R_1 with the concentrations of metal cations in the PAA-PAAM-metal complexes of $W_{PAA} 0.5$.

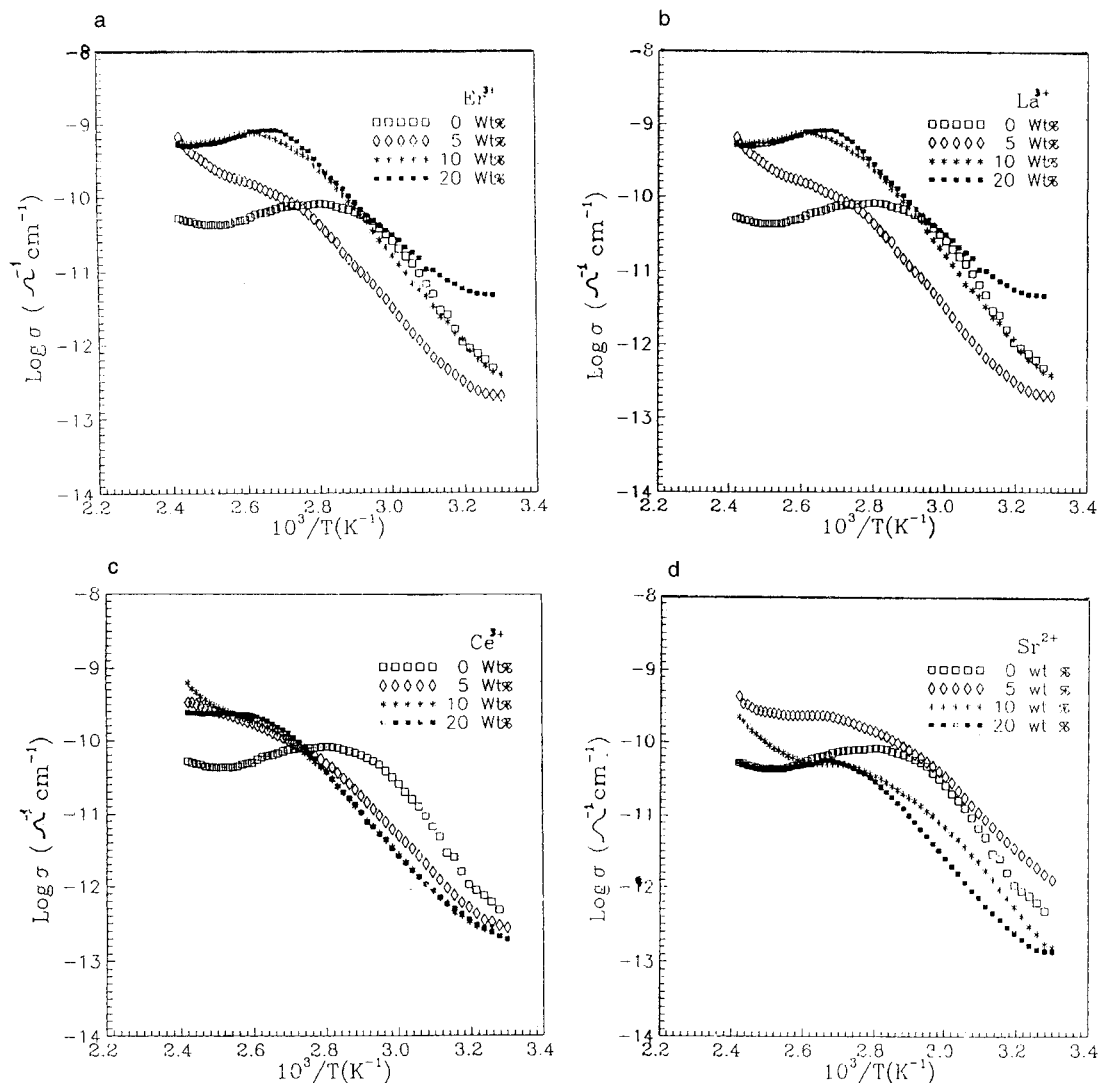


Figure 5 Temperature dependency of log dc conductivity of the PAA-PAAm-metal complexes at $W_{\text{PAA}} = 0.7$: (a) Er^{3+} ; (b) La^{3+} ; (c) Ce^{3+} ; (d) Sr^{2+} .

low pH (2.69), and hydrogen bonding is the primary mechanism of interaction among these polymers.

The present result is in good agreement with the results reported in the literature. Sivadasan et al.⁴ reported that PAA forms a stable complex with PAAm at low pH by using excimer fluorescence and viscosity techniques. They found that analysis of the precipitate confirmed that pyrene-labeled PAAm and PAA formed an equimolar complex at the phase separation pH.

Pradip and Somasundaran³ stated that PAA interacts with PEO and PVP in aqueous solutions through hydrogen bonding and that the interactions between PAA and PVP were stronger than those between PAA and PEO because of the stron-

ger hydrogen-bonding capability of the pyrrolidone group in the PAA-PVP system.

Examples of the FTIR spectra of the dried-powder precipitates of the ternary metal-polymer complexes are presented in Figure 2. Comparison between these spectra revealed that the intensities of the absorption bands, relative to each other, vary from sample to sample according to the weight fraction of the polymers and the concentrations and the physical properties of the metal chlorides. The absorbance A of (C=O) and (C-H) bands at 1700 and 1400 cm^{-1} , respectively, were determined and the ratio R_1 , $A_{(\text{C}=\text{O})}/A_{\delta(\text{C}=\text{O})}$ of these absorbances are plotted against the concentrations of chlorides for the weight fractions $W_{\text{PAA}} = 0.3, 0.5, \text{ and } 0.7$ in Figures 3 and

Table II Relation Between the Activation Energies in the PAA–Metal–PAAm Complexes and the Ionic Radii of the Metals (for 10 wt % and $W_{\text{PAA}} 0.7$)

Ionic Radius (Å)	E_a (eV)
0.0	1.10
0.881 (Er ³⁺)	1.25
1.016 (La ³⁺)	1.11
1.034 (Ce ³⁺)	1.05
1.120 (Sr ²⁺)	1.11

4. It is evident from these figures that R_1 increases or decreases according to W_{PAA} , the concentration and the nature of metal ions. The minimum value is obtained in the presence of $W_{\text{PAA}} 0.3$ and 5 wt % SrCl₂, whereas the maximum value is obtained in the presence of $W_{\text{PAA}} 0.5$ and 5 wt % SrCl₂. The above-mentioned results lead to the conclusion that a ternary metal–polymer complex is formed as a result of the interaction of PAA, PAAm, and metal ions.

The mechanism of conduction in films of PAA, PAAm, and their mixtures and complex was discussed in details in a previous study. The present study deals with the conduction mechanism in films of ternary polymer–metal–polymer complexes.

The variation of the log versus $1/T$ is represented in Figure 5 for various concentrations of the rare-earth metals for $W_{\text{PAA}} 0.7$. This figure shows that conductivity increases with increasing temperature but the rate of increase is different in different temperature regions: it is rapid at low temperatures, slow at moderate temperature, and considerably rapid up to 160°C. It is clear from these figures that above 80°C and for any given concentration of the rare-earth metal chlorides, the conductivity of the metal–polymer complexes is always higher than that of the polymer–polymer complex.

The above-mentioned findings lead to the conclusion that the properties of ternary metal complexes depend on the concentration and physical properties of the metal ions.

Table II shows the relation between the activation energies in the PAA–metal–PAAm complexes and ionic radii of the metals (for 10 wt % and $W_{\text{PAA}} 0.7$). It is obvious from this table that the activation energies of the metal–polymer complexes vary inversely with the increase of the ionic radius. This behavior of changes in the conductivity indicated that the conductivity depends

on the nature, valency, and concentrations of the metals. Moreover, the small changes of the values of the activation energies in these complexes (1.05–1.25 eV) with the ionic radius of metal cations showed that the mechanism of conduction is nearly the same.

From these considerations one can conclude that the tendency of the metals to interact with the PAA–PAAm complexes and to form ternary metal–polymer complexes is nearly the same and the same mechanism of conduction is operating.

CONCLUSIONS

It can be concluded that in the case of PAA–PAAm–metal systems, it was observed that precipitations were formed in these systems and these precipitations were attributed to the formation of ternary metal–polymer complexes as a result of the cointeraction of the metal cations, that is, Er³⁺, La³⁺, Ce³⁺, and Sr²⁺ with the PAA–PAAm complexes. The behavior of change of the absorbances ratio R_1 with the metal cation concentrations depends on the nature of the cation (ionic radius and valency) and on W_{PAA} . The conductivity of the ternary metal–polymer complexes depends on the nature, the valency, and the concentration of metal cations, whereas the variation of the activation energies of conduction was small, indicating that the mechanisms of interaction of these cations with the PAA–PAAm complexes are similar.

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