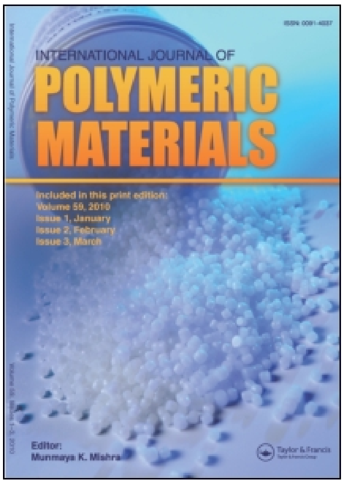

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Change of Polaron Band Width in Polystyrene Composites Containing Transition Metal Halides

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Polystyrene (PS) composite films, containing various fractions of each of $NiCl_2$, $CoCl_2$ and mixtures with Ni or Co powder, were prepared by casting method. The samples were investigated by optical and scanning electron microscopes and differential scanning calorimeter. The temperature dependence of the dc electrical resistivity was interpreted on the basis of the polaron hopping model. The hopping energy states were assumed to be arised from the previously calculated 6-fold symmetric potential barrier due to the phenyl ring rotation. The polaron band width was calculated and its dependence on the filler content was explained.

KEYWORDS: Polystyrene composites, Electron microscopy, Differential scanning calorimetry, Polaron band width.

I. INTRODUCTION

In a previous work[1] we have investigated the effect of Co- and Ni-metal fillers on some physical properties of PS composites. The results of differential scanning calorimetry revealed no change of the main characterising transition temperatures of PS. The free volume conduction mechanism was reasonably used to interpret the dc electrical results. The magnetic results revealed a magnetic role of the polymeric matrix due to the collective states of chain

π-electrons (magnetic solitons) in presence of the ferromagnetic metallic clusters. An *s-d* type magnetic interaction was suggested between the ferromagnetic particles and the solitons in the close vicinity of the particle surface.

The present work concerns with the dependence of the conduction mechanism of PS composites on the type and fraction of fillers. The used fillers are: a) $NiCl_2$ and $CoCl_2$ of 1, 2, 4 and 7.4 wt%, and b) 1% metal halide +3.8, 5.8, 7.6 or 11.8 wt.% metal powder.

II. EXPERIMENTAL

The studied composite films were prepared by casting method.[2] PS material was dissolved in benzene. The desired metal halide ($NiCl_2 + 6H_2O$ or $CoCl_2 + 2H_2O$) was dissolved in ethylalcohol, and then added to the polymer solution. After the mixture attained a suitable viscosity it was cast to a glass dish, and kept in a dry atmosphere at 30°C for two weeks. For the case of metallic additives, the metallic powder was added before casting. The average size of Ni and Co particles were 20 and 40 μm respectively. Several thicknesses were available in the range of $200–600 \pm 5\ \mu$m. The differential scanning calorimetry (DSC) was carried out using a thermoanalyzer type (GDTD 16-Setaram) with temperature range of −193 to 1200°C, heating rate of 9°C/min., and sensitivity 2.50 μV. The electrical measurements were done by standard techniques.[3] The current was measured by means of an electrometer (Levell TM98P) of accuracy ±0.2%. The films were in the form of discs of 1.6 ± 0.001 cm diameter. Contacts were of highly conductive silver paste with an area of 1 cm^2. A guard ring was used. The sample was short circuited for about two days, at a constant temperature (308 K), before the dc voltage was applied. The current was independent on time and the current voltage characteristics exhibited an ohmic behaviour, in the studied voltage range (0–400 V). This implied that there was no ionic conduction.

III. RESULTS AND DISCUSSION

III.A. Optical microscopy

Figure 1 depicts the micrograph of PS composite doped with 1% $NiCl_2$ and loaded with 5.8% Ni powder. The fine Ni-particles are

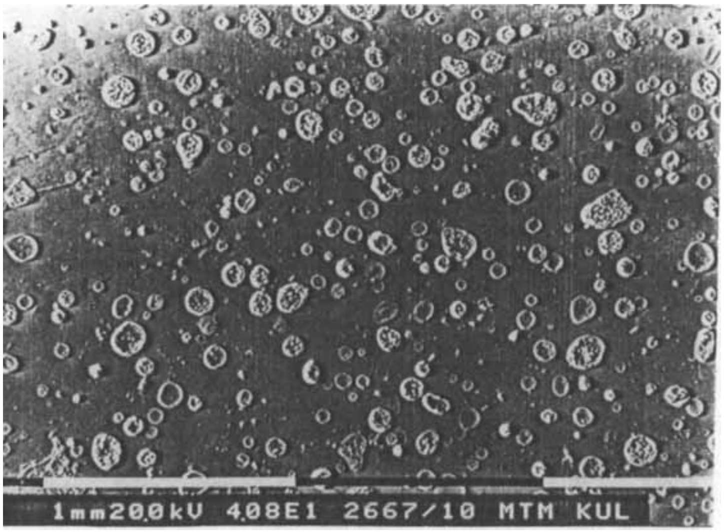

FIGURE 1 Micrograph of PS doped with 1% $NiCl_2$ and loaded with 5.8% Ni. Magnification 40.8×.

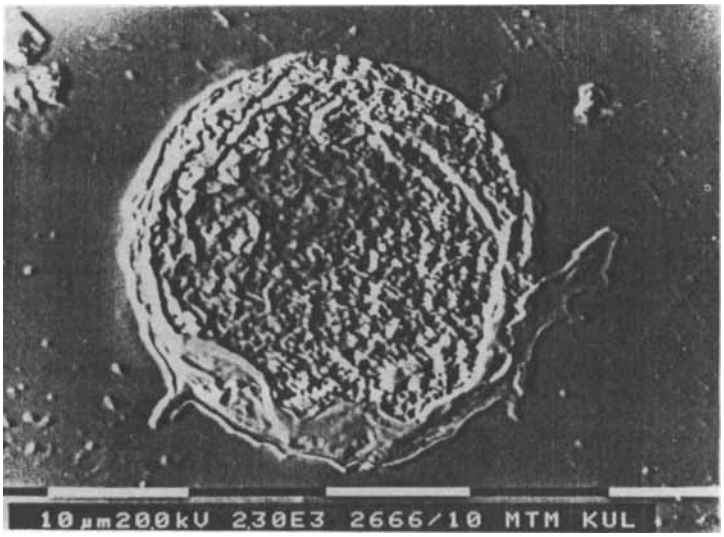

FIGURE 2 Micrograph of the separated $NiCl_2$-rich phase as a circular patch within PS. Magnification 2300×.

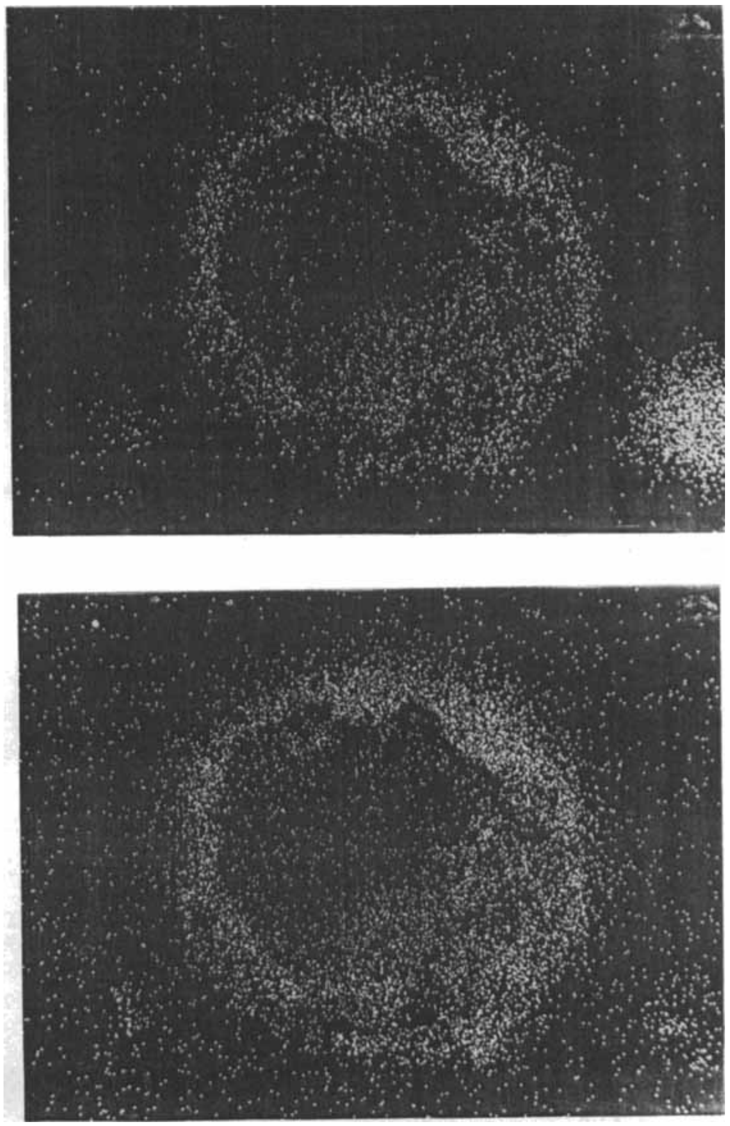

FIGURE 3 a) Ni-map and b) Cl-map of the patch presented in Figure 2.

distributed on the composite surface. Nearly circular patches, of size >Ni-particles, are separated. Figure 2 presents a highly enlarged micrograph of one of these patches, for which Ni- and Cl-maps are presented in Figures 3a, b. The last two figures suggest that the observed patches belong to a $NiCl_2$-rich separated phase.

Figure 4 presents the micrograph of PS composite doped with 1% $CoCl_2$. It is implied that this micrograph contains three phases:

a) a continuous (halide poor) polymeric matrix,

b) separate halide rich domains (HRD) distributed within the continuous phase, and

c) secondary separated spheroidals (of highly concentrated halide) spreaded inside the HRD. Figures 5a–b indicate that as the $CoCl_2$ content increases the HRDs grow on the expense of the continuous phase.

It could be concluded from the above microscopical analysis that the loading with metallic powders and doping with metallic halides result in morphological changes. These changes may influence the other physical properties of the composites.

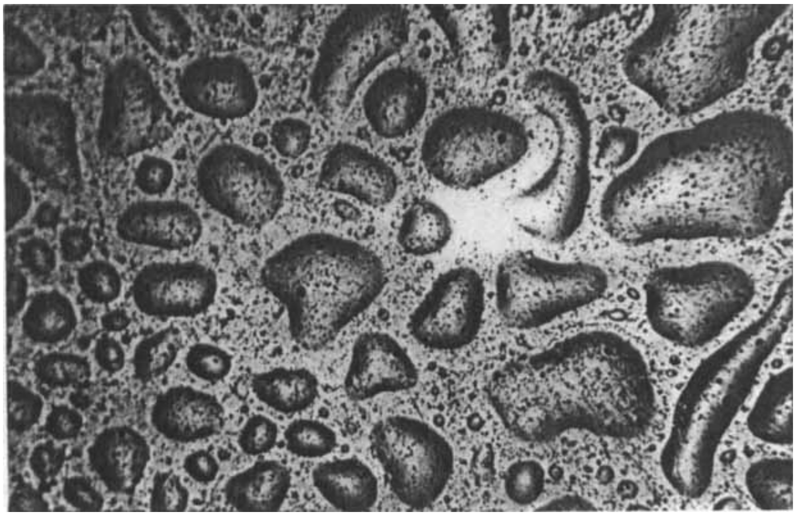

FIGURE 4 Micrograph of PS containing 1% $CoCl_2$. Magnification 800×.

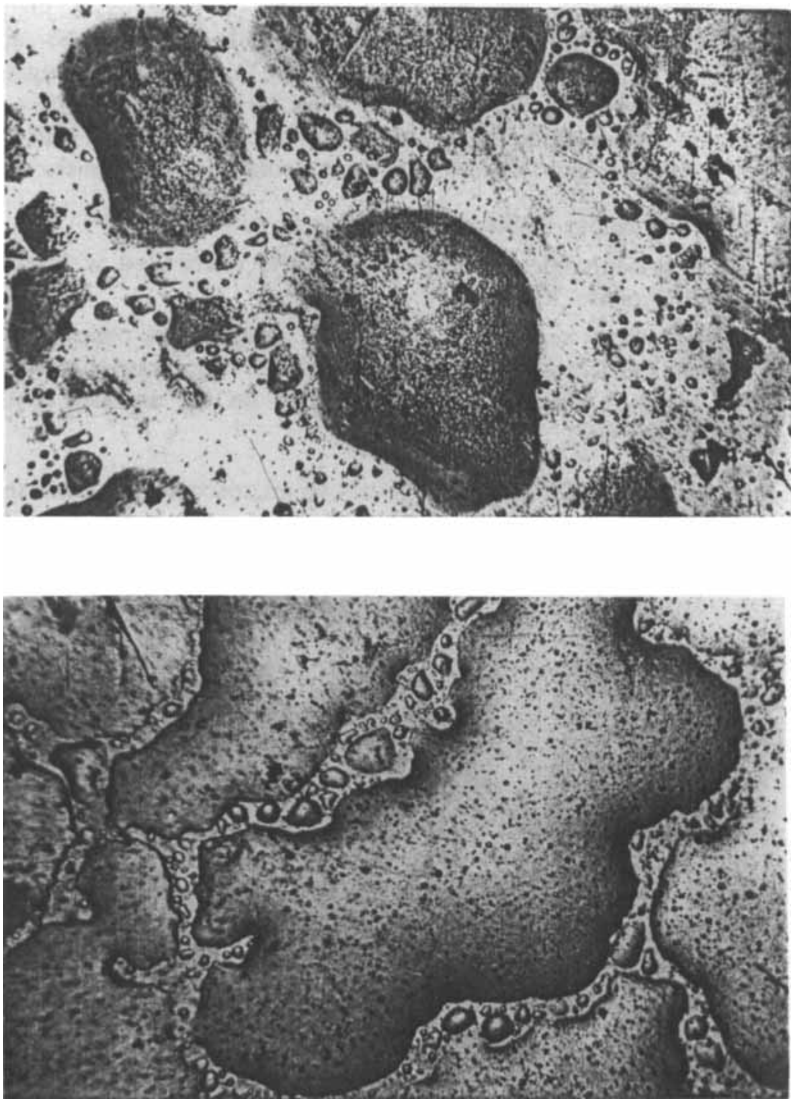

FIGURE 5 Micrographs of PS containing: a) 4 and b) 7.4% $CoCl_2$. Magnification 800×.

III.B. Thermal analysis

Figure 6 shows the DSC plots for PS doped with various weight fractions of $CoCl_2$. It is noticed that the plots exhibit the same characterizing transition temperatures. The observed transitions can be assigned as follows. The *Tw* exotherms (at 302–307 K) are due to the small amount of water which is always present in the conventional polymer unless it is carefully vacuum dried. Water also has a plasticizing effect in PS which appears as a shift of *Tg* to lower temperature.[4] The *Tgg* endotherms (at 317–320 K) may be arised from the wagging motion of the phenyl ring.[5] The Tg_1 and Tg_2 endotherms (at 330–332 K and 355–360 K) can be assigned to the glass rubber transition of the halide poor- and halide rich phases respectively.[6] At the T_l endotherms (at 407–420 K) the viscoelastic fluid becomes viscous.

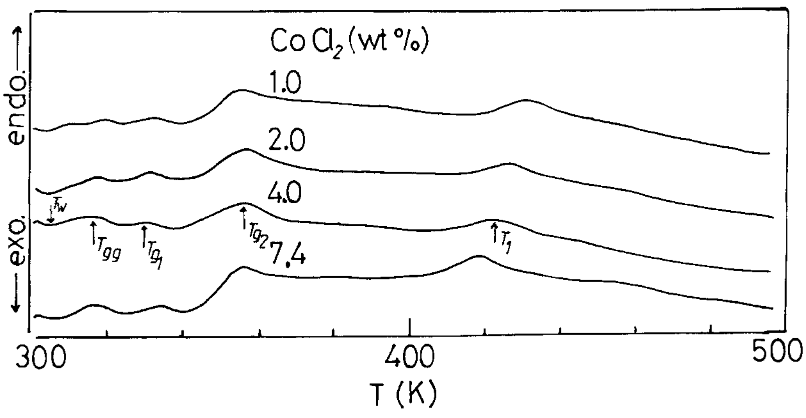

FIGURE 6 DSC plots for PS containing: 1, 2, 4 and 7.4% $CoCl_2$.

III.C. Electrical resistivity of PS doped with transition metal halides

Figure 7 depicts the reciprocal temperature dependence of $\ln \rho$ for PS doped with $CoCl_2$. The polymeric temperature region can be expressed by the Arrhenius equation in which

$$\rho = \rho_0 \exp(E/kT), \tag{1}$$

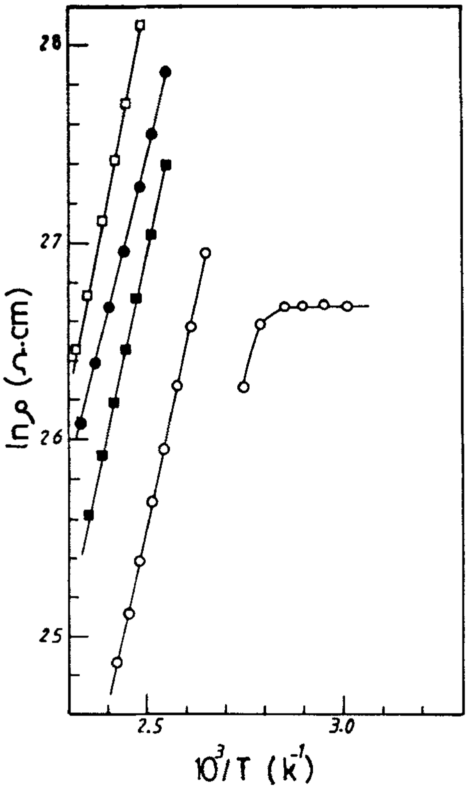

FIGURE 7 Arrhenius plots for PS containing: (●)1, (□)2, (○)4, (■)7.4% $CoCl_2$.

where ρ_0 is constant, E is the activation energy, k is the Boltzmann's constant. The effect of halide content on $\ln \rho$ (measured at 411 K) and E are presented in Figure 8. It is clear from this figure that E exhibits a relatively small value within the range of 15.4 to 22.3 Kcal/mol. Maxima were observed, for E and $\ln \rho$, at 2% dopant. For dopants <1% ρ does not follow E. Moreover the dc polarization current, which characterises the ionic conduction, was not observed for the studied composites. The current density (J_1) was measured as a function of thickness (d) and $J_1 - d^{-3}$ dependence was not observed. This result, together with the mentioned linear I–V characteristics, ruled out the predominance of a space charge mechanism. The obtained linear I–V dependence

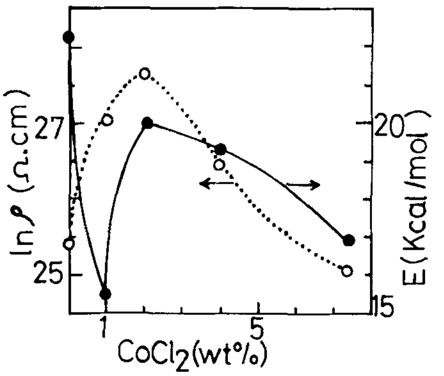

FIGURE 8 Dependence of ln ρ and E on $CoCl_2$ contents in PS composites.

also ruled out the predominance of Schottky mechanism. This is because for such mechanism to operate one must obtain a dependence of the form $\ln J_1 \propto V^{1/2}$, which is not observed.

These observations suggest the application of the mechanism of small polaron hopping, proposed by Austin and Mott,[7] between equilibrium energy states of different values. It is thought that the different energy states, in our case, may arise from the wagging motion of the phenyl ring[5] in the chlorine-substituted PS due to the halide doping effect. Reich and Eisenberg[8] calculated the hindered rotation of the phenyl ring in polystyrene by assuming 6-fold symmetric potential barrier. The calculated potential as a function of the rotation angle has the extreme values of 4.5–13 Kcal/mol and the calculated transition frequency for ring rotation was 10^{12} and 10^{13} Hz ($\simeq \nu_0$, which is the optical phonon frequency) for barrier energy 8.0 and 4.5 Kcal/mol respectively, at temperature = 380 K.

The following equation for dc resistivity, in the polaron hopping mechanism, was proposed by Austin and Mott:[7]

$$\rho = \frac{akT}{\nu_0 c(1-c)e^2} \exp(2 \propto a) \exp(E/kT), \tag{2}$$

where c is the fraction of reduced transition metal ion, a is the mean spacing of the hopping sites, e is the electronic charge and $\propto$ is the tunneling factor. In this model E can be given by

$$E = E_H + \tfrac{1}{2}E_D, \tag{3}$$

where E_H and E_D are the hopping and disorder energies. Usually[9] $E_D < E_H$ and $E \simeq E_H$.

Eq. (2) can be reduced to Eq. (1) if we put

$$\rho_0 = \frac{akT}{\nu_0 c(1-c)e^2} \exp(2 \propto a) \tag{4}$$

For the adiabatic small-polaron hopping, the activation energy can be described using the polaron band width, J, as follows:[10]

$$E \simeq E_H = \tfrac{1}{2}E_p = \tfrac{1}{2}(E'_p - 2J), \tag{5}$$

where E_p is polaron binding energy and E'_p is the maximum polaron binding energy (the maximum value of E in the composition range of electron conduction). It is found that J is proportional to $1/a$. The conditions of adiabatic and nonadiabatic hopping can be described with polaron band width J as the following inequalities respectively:[11]

$$J > [2kTE'_H/\pi]^{1/4}[h\nu_0/\pi]^{1/2}, \tag{6}$$

$$J < [2kTE'_H/\pi]^{1/4}[h\nu_0/\pi]^{1/2}. \tag{7}$$

Assuming ν_0 to be 10^3 Hz, the values of the right hand side of the inequalities (6,7) were estimated to be 2.65 Kcal/mol, for $CoCl_2$ dopants. The corresponding value of E'_H was taken as 20 Kcal/mol, the maximum value of E in Figure 8. The value of J were calculated, using Eq. (5), and the dependence of J on $CoCl_2$ contents are plotted in Figure 9.

It would be concluded that the polaron band-width, J, affects mainly the conduction regime of the present composites. In the

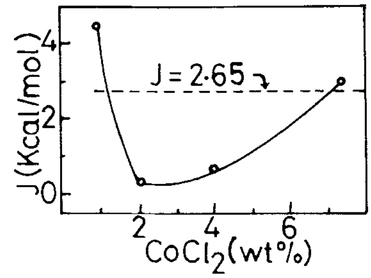

FIGURE 9 Polaron band width as a function of the halide contents in PS.

adiabatic region, J was wide and the transition probability was as high as the optical phonon frequency ($\simeq 10^{13}$ Hz), and the tunnelling process could be neglected. On the other hand in the nonadiabatic region J became narrower and the transition probability was much less than ν_0, and the tunneling process became important.

III.D. The dc conduction of PS containing transition metals and their halides

Figure 10 shows the Arrhenius plots of $\rho(T)$ for PS doped with 1% $NiCl_2$ and loaded with 3.8, 5.8, 7.6 and 11.8% Ni powder. Similar plots were obtained for $CoCl_2$ dopant and Co filler but they are not presented here. The effect of metal content (M), where M refers to Ni or Co, on E and ρ (measured at 411 K) are plotted in Figure 11. It is clear from these plots that $\ln \rho$ follows E. A maximum of E is observed at $M = 3.8\%$ and a minimum is observed at $M = 7.6\%$. The small polaron hopping regime could be applied in the present case. The presence of metallic particles in the polymeric matrix results in the following:

i) a shortening of the main polymeric chain,[12] which leads to an increase of E and ρ,

ii) a formation of a more rigid network in the boundary layer surrounding the filler particle,[13] which also increases E and ρ; and

iii) according to the Maxwell–Wagner–Sillar's (MWS) model,[14] the negatively charged metallic particles (due to the external field) induce a volume charge distribution around their surfaces. These positively charged volumes enhance the migration of the conduction electrons which results in the decrease of E and ρ.

The initial increase of E for $M < 3.8\%$, in Figure 11, may be arised from the first two effects, while the observed decrease of E for $3.8 \leqslant M \leqslant 7.6\%$ can be attributed to the predominance of the third effect. For $M > 7.6\%$ the MWS induced positively charged volumes may act as trapping centres for the conduction electrons. Thus two effects may be arised: a) a neutralization of some of the MWS induced positively charged volumes, and b) a decrease in the density of the conduction electrons. These two effects may interpret the observed increase of E for $M > 7.6\%$.

Using Eq. (5) the polaron band width J was calculated and the

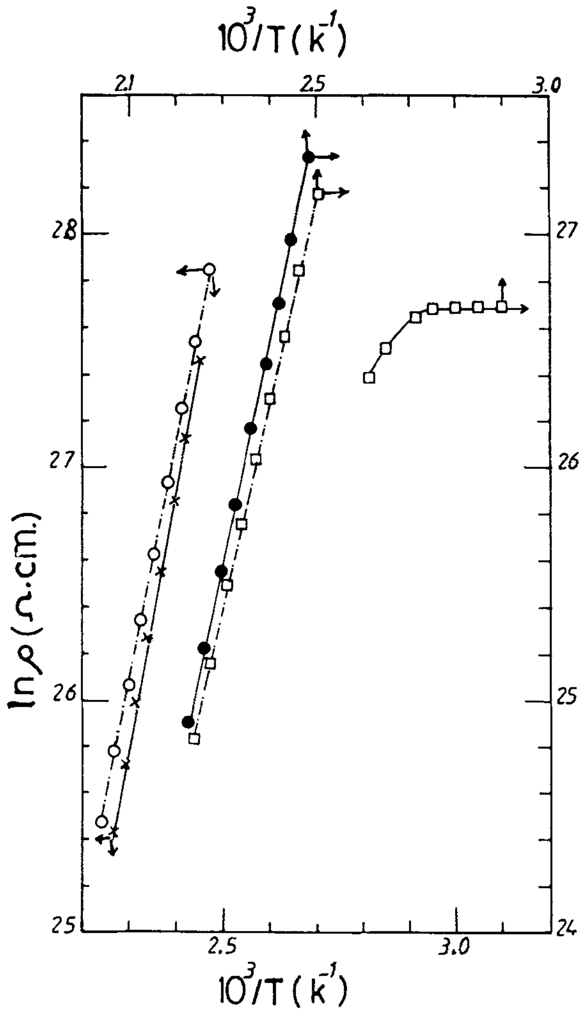

FIGURE 10 Arrhenius plots for PS containing 1% $NiCl_2$ and: (○)3.8, (●)5.8, (□)7.6 and (×)11.8% Ni.

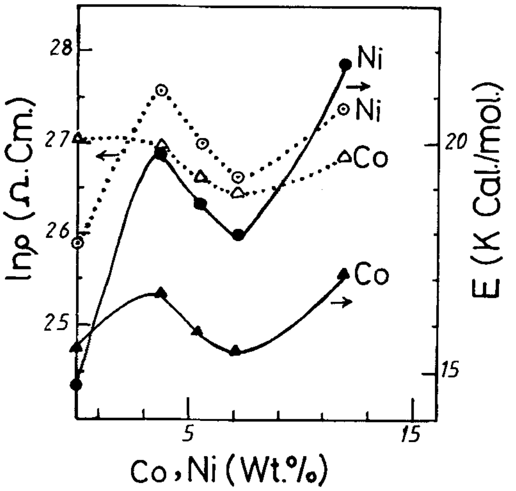

FIGURE 11 The dependence of ln ρ and E on the metal content in PS.

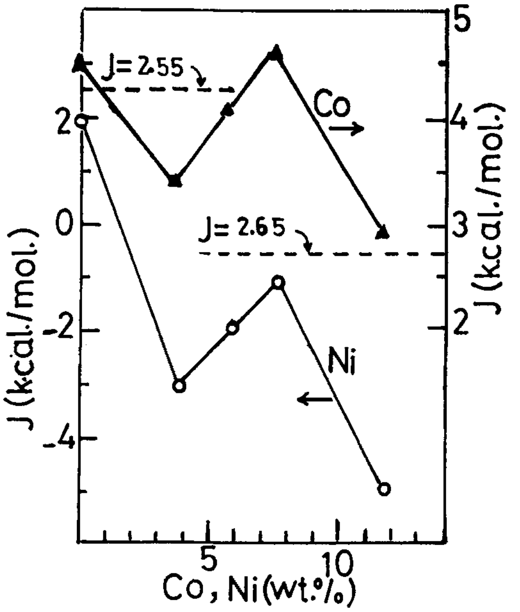

FIGURE 12 The effect of metal content on the polaron band width in PS.

results were plotted as functions of M, in Figure 12. For the case in Ni-containing composites, Figure 12, the J values exhibit a fluctuating behaviour and satisfy the nonadiabatic (tunneling) condition. Moreover the observed negative J-values means that the polaron centre pinned at the impurity site gives the equilibrium position.[15] For the case of Co-containing composites, Figure 12, all of the J-(fluctuating) values satisfy the adiabatic condition.

It could be concluded that the polaron band width is affected by:

a) the type and fraction of the doping halide, and

b) the fraction of the loading metal.

However, the reason of the fluctuating behaviour of J is not clear so far. Further detailed investigations are in progress.

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