Chapter V

Results and Discussion

electron jumping (hopping or tunneling) between filled and empty sites localized in the energy band gap. Due to the deficiency in the concentration of doped materials (i.e. absence or decrease in the concentration of n- or p-materials in the pure PMMA), the PMMA has low conductivity and behaves as an insulator material.

V-A-1-ii. PMMA-dye samples:

For polymer-dye samples investigated, the temperature dependence of DC-conductivity is shown in Fig. (V-A-1). The plot of ln σ_{DC} vs. 1/T shows the same behavior as that observed for pure polymer in the lower and higher temperature range in addition to a break in conductivity is observed at 343 K for P_1. At each temperature, the conductivity values for all polymer-dye samples are higher than that of the pure PMMA. This indicates that the introducing dye in the polymer matrix may act as localized centers affecting the conduction process [29] in PMMA.

According to the chemical structure of the dyes investigated, the conductivity data can be divided into different groups according to the following:

For (P_8, P_9, P_{10}), which show an identical chemical structures Fig.(V-A-1), σ_{DC} at 353 K was found to increase in the order, Table (V-1):

$$P < P_{10} < P_9 < P_8$$

This order can be attributed to the more enrichment of electrons in the dyes by the presence of methoxy group in P_8 than hydroxy in P_9 and methyl group in P_{10}.

For (P_4, P_5, P_6)

$$P < P_4 < P_5 < P_6$$

Table (V-1): DC-conductivity data for investigated samples.

Samples	σ * ohm^{-1},cm^{-1}	E_a (eV)	Temp. Range # (K)
P	$4.63x10^{-12}$	0.44	343-373
P_1	$3.45x10^{-11}$	0.18	343-363
P_2	$2.68x10^{-11}$	0.20	353-373
P_3	$7.25x10^{-12}$	0.31	333-373
P_4	$6.24x10^{-12}$	0.33	333-373
P_5	$1.08x10^{-11}$	0.28	323-373
P_6	$5.63x10^{-11}$	0.24	323-363
P_7	$6.24x10^{-12}$	0.33	343-373
P_8	$1.38x10^{-11}$	0.32	333-373
P_9	$6.89x10^{-12}$	0.38	343-373
P_{10}	$5.64x10^{-12}$	0.40	343-373
P_{11}	$4.76x10^{-11}$	0.21	353-373
P_{12}	$8.01x10^{-12}$	0.33	343-373

* σ_{DC} at 353 K.

Temperature range at which the activation energy, E_a, was calculated.

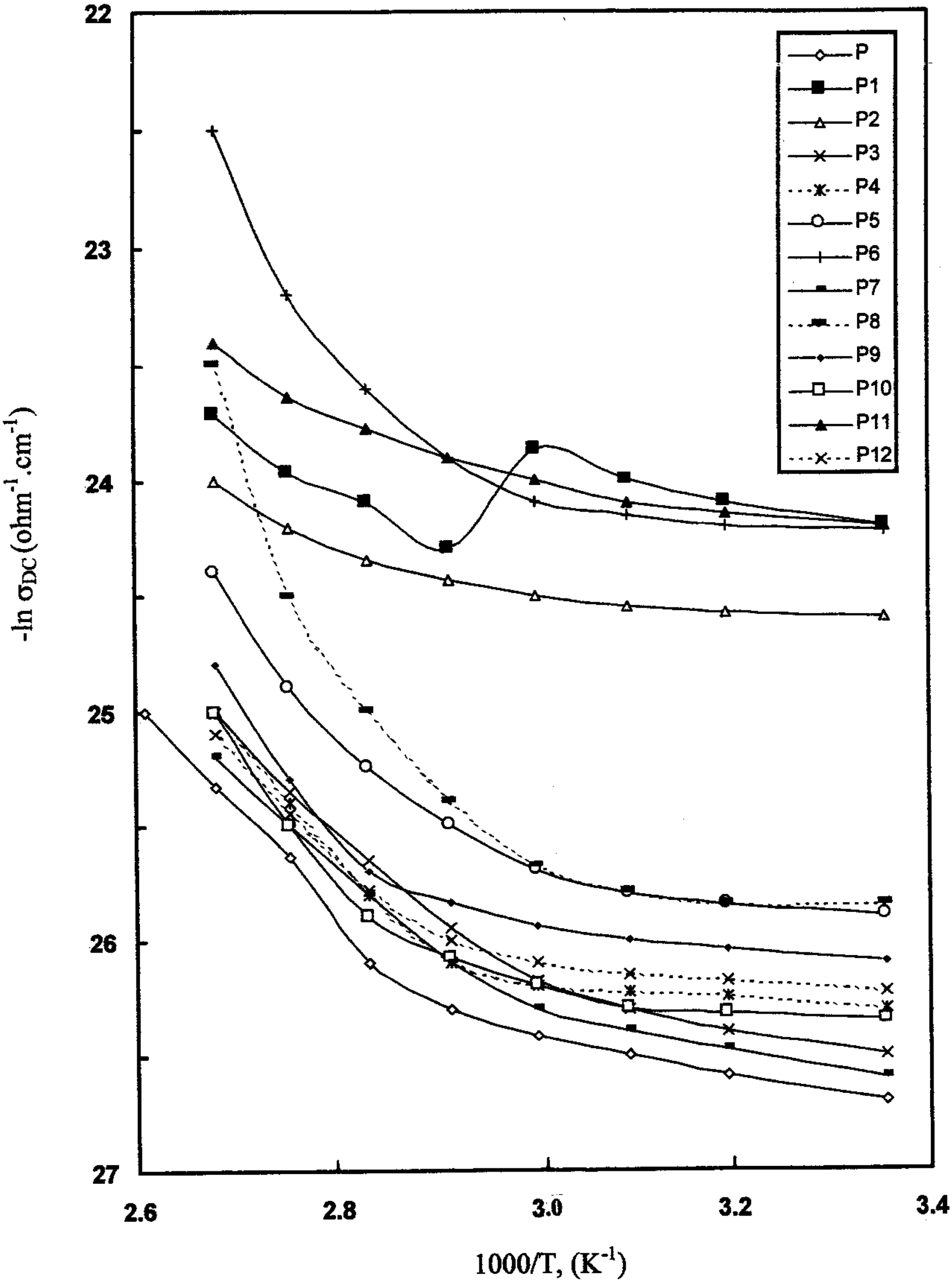

Fig. (V-A-1): Effect of temperature on electrical conductivity (σ_{DC}) for all investigated samples.

electron jumping (hopping or tunneling) between filled and empty sites localized in the energy band gap. Due to the deficiency in the concentration of doped materials (i.e. absence or decrease in the concentration of n- or p-materials in the pure PMMA), the PMMA has low conductivity and behaves as an insulator material.

V-A-1-ii. PMMA-dye Samples:

For polymer-dye samples investigated, the temperature dependence of DC-conductivity is shown in Fig. (V-A-1). The plot of ln σ_{DC} vs. 1/T shows the same behavior as that observed for pure polymer in the lower and higher temperature range in addition to a break in conductivity is observed at 343 K for P_1. At each temperature, the conductivity values for all polymer-dye samples are higher than that of the pure PMMA. This indicates that the introducing dye in the polymer matrix may act as localized centers affecting the conduction process [29] in PMMA.

According to the chemical structure of the dyes investigated, the conductivity data can be divided into different groups according to the following:

For (P_8, P_9, P_{10}), which show an identical chemical structures Fig.(V-A-1), σ_{DC} at 353 K was found to increase in the order, Table (V-1):

$$P < P_{10} < P_9 < P_8$$

This order can be attributed to the more enrichment of electrons in the dyes by the presence of methoxy group in P_8 than hydroxy in P_9 and methyl group in P_{10}.

For (P_4, P_5, P_6)

$$P < P_4 < P_5 < P_6$$

V-A-2. AC-Electrical Conductivity:

For the investigated samples the AC-electrical conductivity as a function of the reciprocal of absolute temperature for the investigated samples has been also studied at different frequencies ranging from 30 – 1000 kHz. The results are represented by potting ln σ_{AC} vs. 1/T, Figs. (V-A- (2-8)).

The AC-conductivity can be expressed according to Eq. (II-12) [87]:

$$\sigma_{total} = \sigma_{AC}(\omega) + \sigma_{DC} \quad (V.3)$$

where $\sigma_{AC}(\omega)$ is the polarization conductivity and depending on the measuring frequency according to Eq. (II-13):

$$\sigma_{AC}(\omega) = A\,\omega^{s} \quad (V.4)$$

where A is constant and s is an exponential power of frequency (ω). Generally, the electrical conduction occurring in amorphous semiconductor such as in our case would be due to [24] (i) band conduction, similar to that of a crystalline semiconductor (ii) conduction in localized states at the edge of the valence and conduction band or (iii) conduction in localized states near Fermi level, see Chap. II.

The main models developed to account for the frequency dependence of $\sigma_{AC}(\omega)$ are:

(a) the quantum mechanical tunnelling (QMT) model.

(b) the hopping over barrier (HOB) model.

Based on QMT model, Austin and Mott [82] explain $\sigma_{AC}(\omega)$ behaviour with frequency as due to electron tunnelling between the localized states lying deep within the energy gap. The HOB model was suggested by Pike [83] where hopping is considered to be over a barrier (W) within the localized band while excitation to conduction band has a different barrier (W_M). Assuming the hopping between adjacent pairs, randomly distributed with different barrier heights, Elliot [86,119] suggested a relation between $\sigma_{AC}(\omega)$ and the slope s. According to these model, s should be temperature dependent and should decrease with increasing temperature.

V-A-2-i. Pure PMMA:

The temperature dependence of AC conductivity for pure PMMA at different frequencies (30 – 1000 kHz) is shown in Fig. (V-A-2). The conductivity has been found to increase with frequency and temperature till T = 373 K before starting to decrease with further heating. This can be explained according to the fact that, AC-conductivity arises from the rapid transitions between localized states of charge species such as electrons or dipoles. So at 383 K, either thermal energy disturbs dipole transitions or a phase transition has occurred to a phase of lower conductivity value [29]. Because the DTA thermogram did not show any phase transition at this temperature; in addition to that the plot of ln σ_{DC} vs. 1/T did not show also any break at 383 K, so the change in σ_{AC} at 383 K is attributed to the disturb occurring in the dipoles arrangement in the sample. The conductivity values obtained for PMMA is comparatively low. This could be interpreted on the basis that the dipole in long chain polymer is not quite free to rotate but is constrained to assume discrete orientations with respect to its nearest – neighbours, in the amorphous state. As this acrylate is strongly disordered structurally in the amorphous state, comparatively weak polarization may result from hopping of charge carriers; which perhaps accounts for the low value of AC-conductivity of this polymer [24].

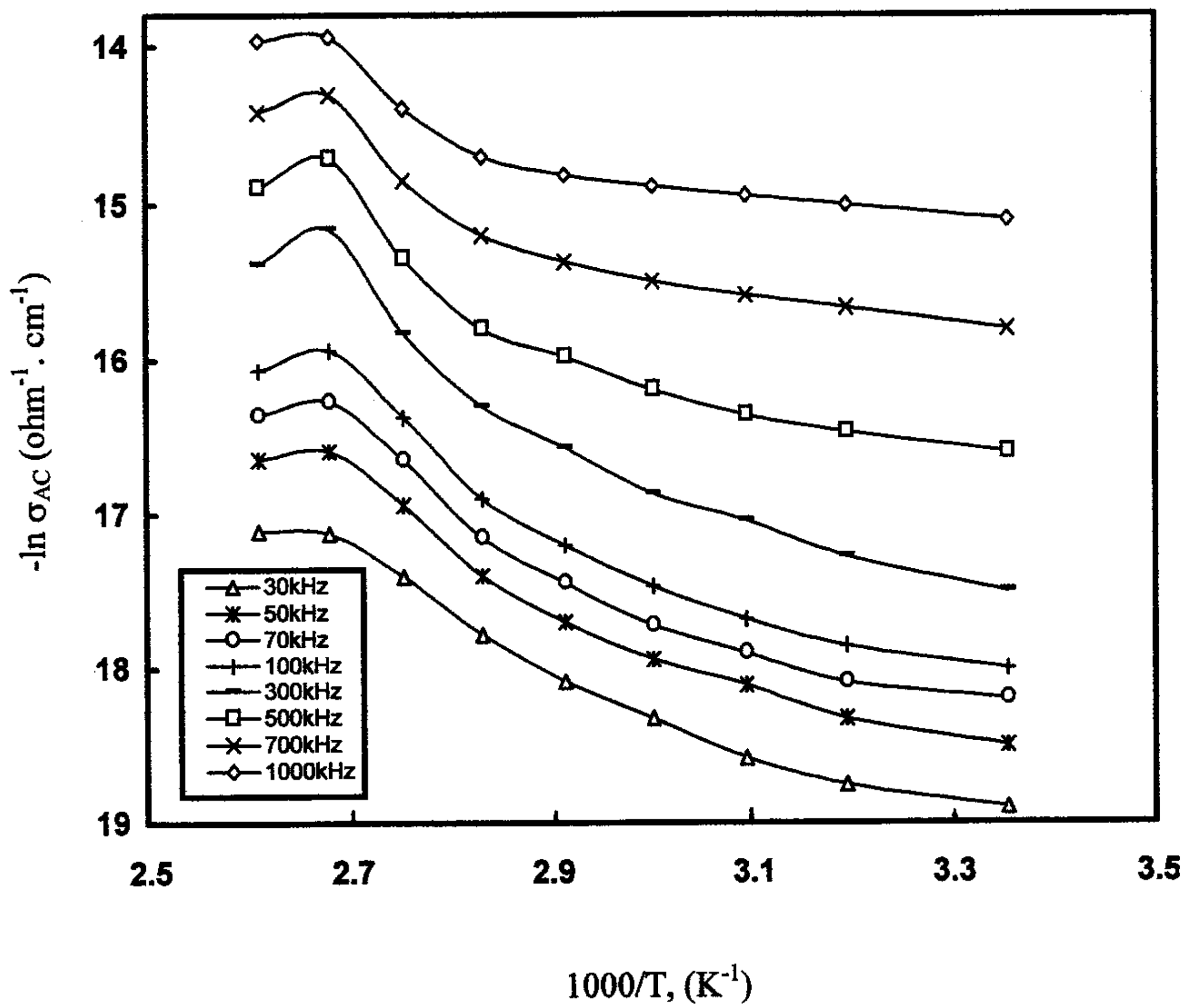

Fig. (V-A-2): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for pure PMMA.

V-A-2-ii. PMMA-dye Samples:

For PMMA-dye samples the temperature dependence of AC-conductivity at different frequencies (30 – 1000 kHz) is shown in Figs. (V-A- (3-8)). The plot of ln σ_{AC} vs. 1/T for all polymer-dye samples exhibite the same trend as that of the pure PMMA, where at lower temperature region 298 < T < 333 K σ_{AC} is slightly increase with temperature while at higher temperature T > 333 K σ_{AC} is rapidly increase with rising temperature. Generally, for all polymer-dye samples σ_{AC} was found to be higher than that of σ_{DC} referring to the presence of polarization effect. The σ_{AC} values are higher than those obtained for pure PMMA which can be attributed to the large dipole of dye content. The drop in σ_{AC} value at T = 343 K for P_1, P_5 and a T = 353 K for P_{10}, P_4 indicating that at these temperatures, thermal energy disturb the dipole arrangement occurred in the samples or a phase transition has occurred to a phase of lower conductivity value [29]. The conductivity data are summarized and given in Table (V-2). The increase in σ_{AC} with increasing ω (ω = 2πF, where F is the frequency) indicates that the hopping mechanism dominates in the investigated samples. Also the oscillation field accompanied with frequency would be increasing and will lead to an increase in the polarization of the samples appearing in that the form of conductivity increases.

From this Table (V-2), the arrangement of σ_{AC} within the samples with similar chemical structure shows that σ_{AC} at 353 K and 100 kHz, Fig. (V-A-9), increases in the following order:

For (P_8, P_9, P_{10})

$$P < P_{10} < P_9 < P_8$$

For (P_1, P_2, P_3, P_7)

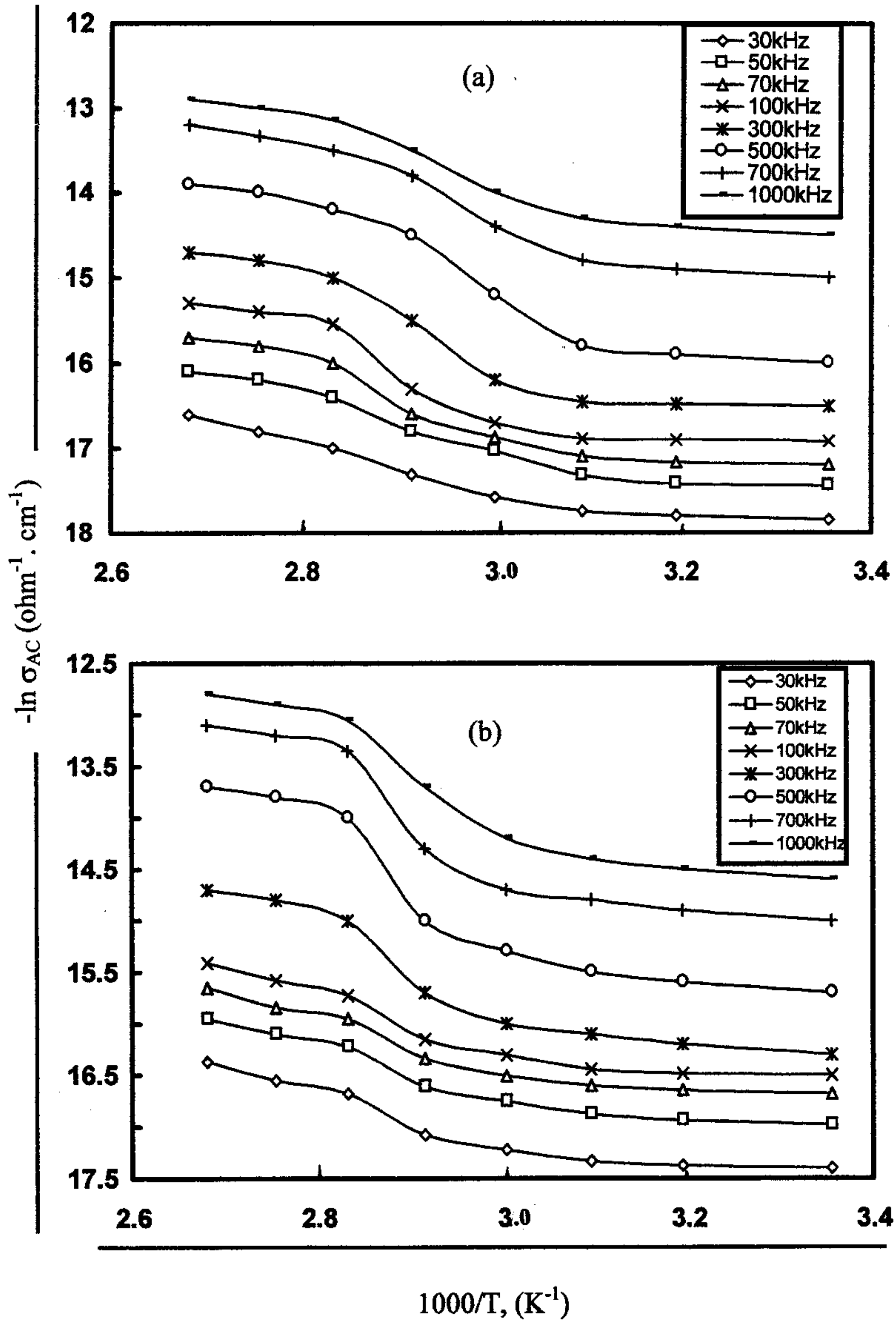

Fig. (V-A-3): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for P_{11} (a) and P_{12} (b).

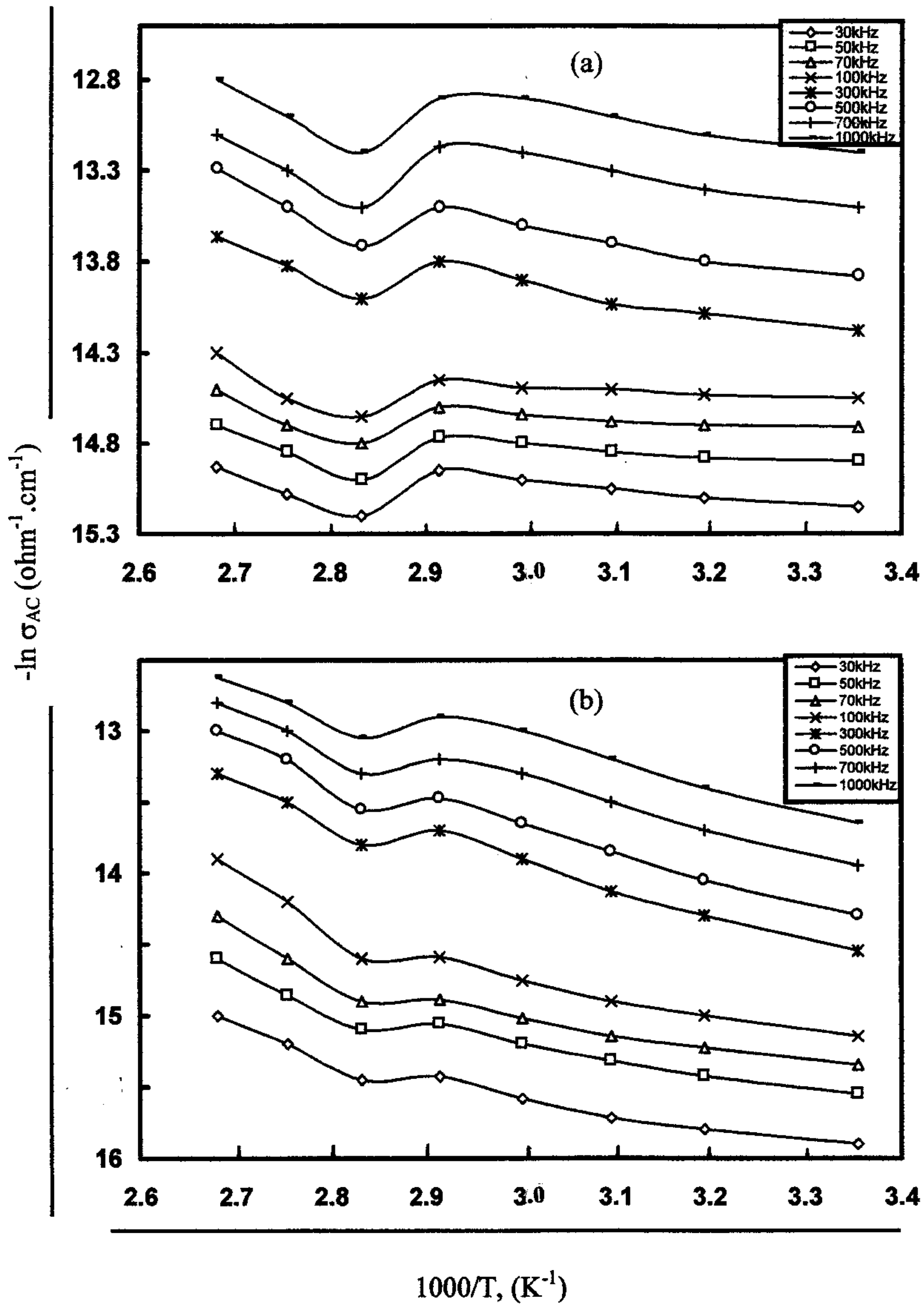

Fig. (V-A-5): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for P_4 (a) and P_{10} (b).

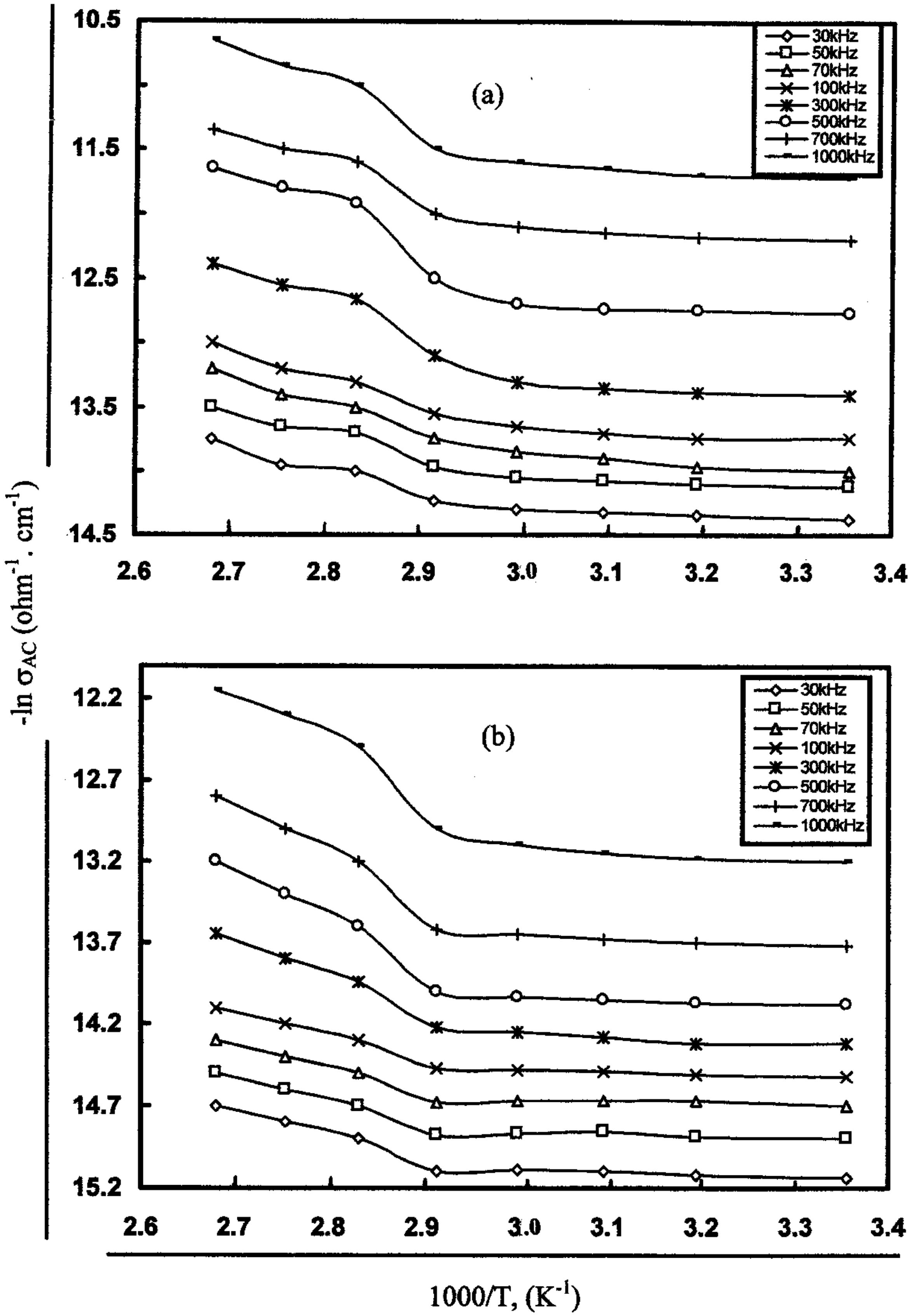

Fig. (V-A-6): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for P_8 (a) and P_9 (b).

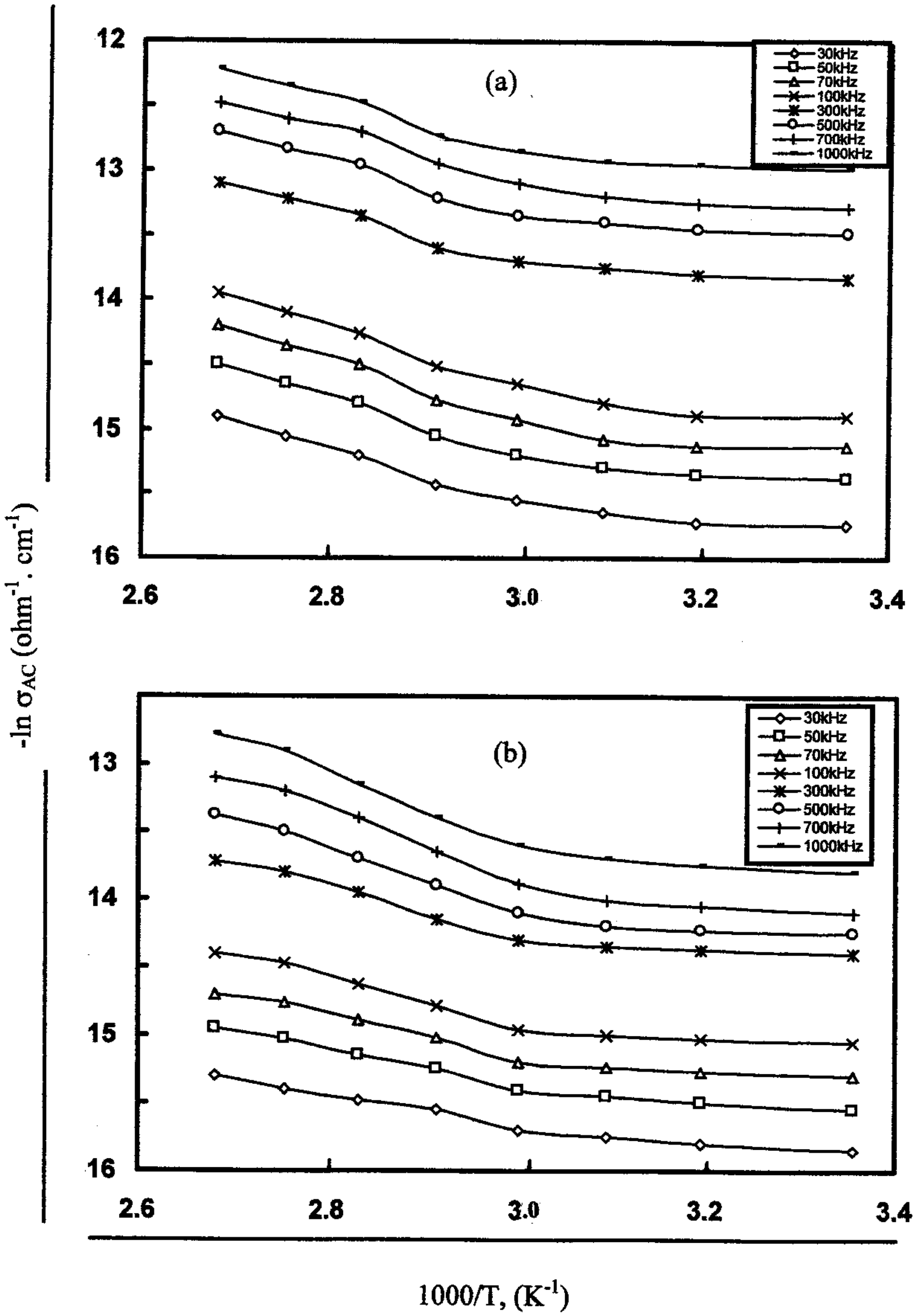

Fig. (V-A-7): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for P_2 (a) and P_3 (b).

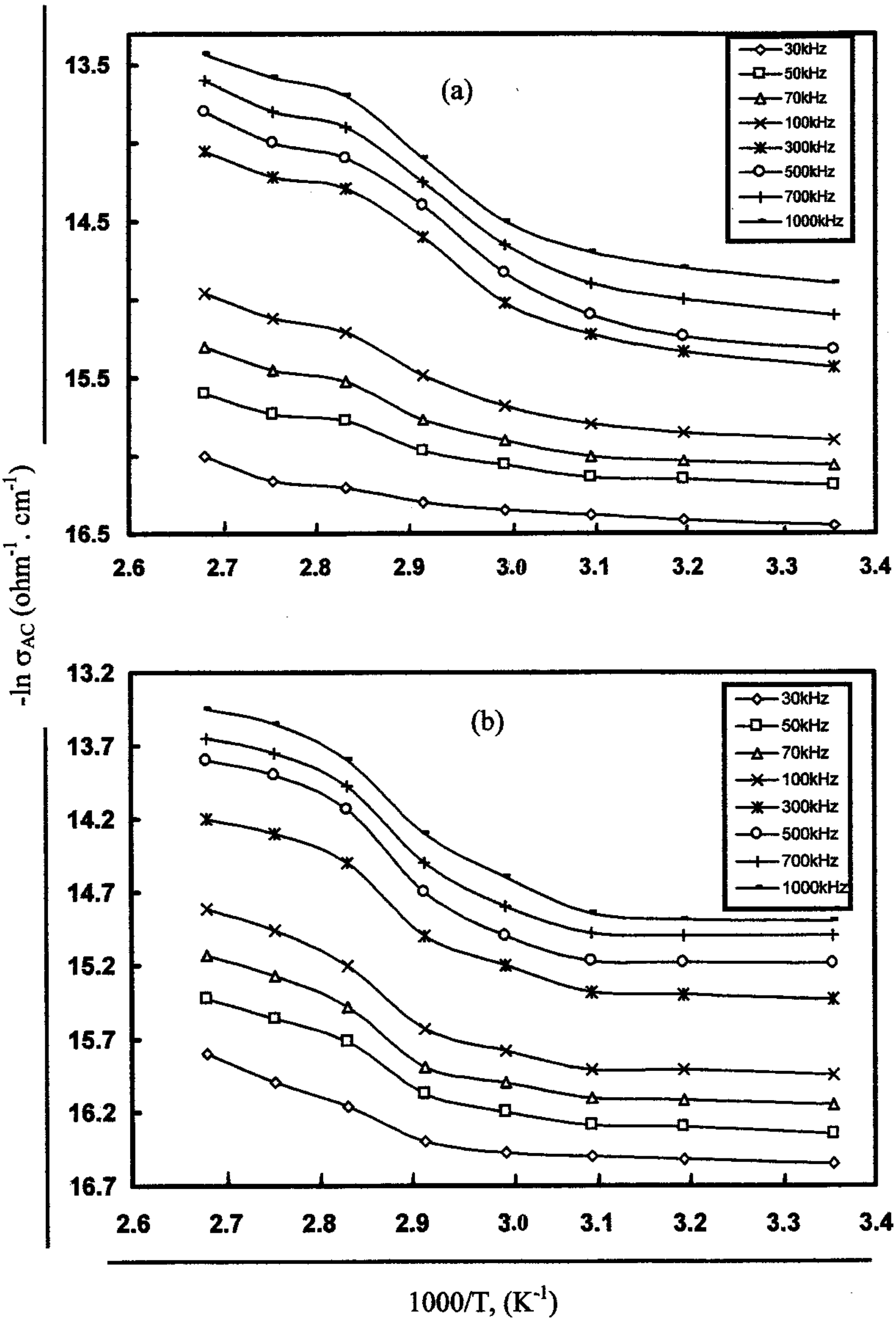

Fig. (V-A-8): Effect of temperature on electrical conductivity (σ_{AC}) (at different frequencies) for P_6 (a) and P_7 (b).

The values of s were determined by plotting Log σ_{AC} vs. Log ω. The values of exponent s are listed in Table (V-2). The hopping over barrier (HOB) model predicts lowering in s values with temperature Eq. (II-21), which is observed in our study for all the investigated samples.

According to the HOB model, the Coulomb well barrier of charge carriers, which are separated by interstice R, overlap causing in a lowering of the effective barrier to W_M Eq. (II-21),

$$s = 1 - \left\{ \frac{6 k_B T}{W_M} \right\} \qquad (V.5)$$

The overlap increases with increasing the temperature. The values of W_M can be obtained by plotting s versus T, Fig. (V-A-10). The values obtained are listed in Table (V-2). This Table shows that the effective barrier W_M for polymer-dye samples increases in the following order:

For (P_8, P_9, P_{10})

$$P_9 < P_8 < P_{10} < P$$

For (P_1, P_2, P_3, P_7)

$$P_3 < P < P_2 < P_7 < P_1$$

For (P_4, P_5, P_6)

$$P_4 \simeq P_6 < P_5 < P$$

For (P_{11}) and (P_{12})

$$P_{11} < P_{12} < P$$

Adding P_8, P_9, P_{10}, P_4, P_5, P_6, P_{11}, and P_{12} dyes to pure polymer lowering its barrier, while addition of P_1, P_2, and P_7 increase its barrier due to large size of these dyes. Low value of W_M for P_3 than PMMA can be attributed to the presence of pyrimidine ring.

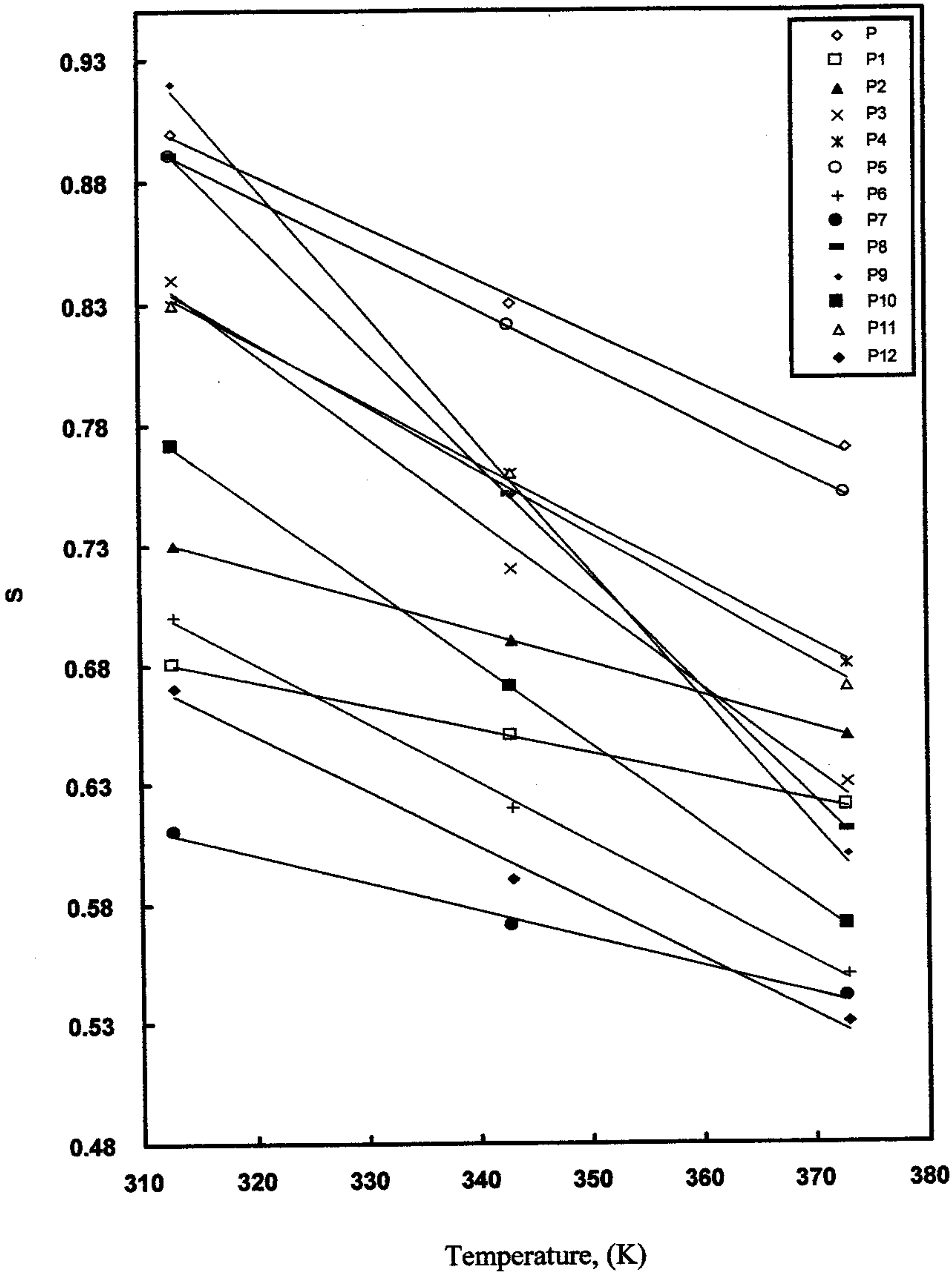

Fig. (V-A-10): Effect of temperature on s value for all investigated samples.

Table (V-2): AC-conductivity data for investigated samples.

Samples	F	E_a (eV)	# Temp. Range (K)	W_M (eV)	* σ $ohm^{-1}.cm^{-1}$	$ s At Temp. Range (K)		
						313 K	343 K	373 K
P	30 kHz 100 kHz 1000 kHz	0.36 0.32 0.31	343-373 323-363 343-373	0.23	$4.8x10^{-8}$	0.91	0.83	0.78
P_1	30 kHz 100 kHz 1000 kHz	0.13 0.11 0.10	363-373 363-373 343-353	0.49	$1.4x10^{-6}$	0.68	0.65	0.62
P_2	30 kHz 100 kHz 1000 kHz	0.15 0.13 0.11	313-353 313-353 353-373	0.37	$6.0x10^{-7}$	0.73	0.69	0.65
P_3	30 kHz 100 kHz 1000 kHz	0.15 0.14 0.12	333-373 333-373 363-373	0.14	$4.0x10^{-7}$	0.84	0.72	0.63
P_4	30 kHz 100 kHz 1000 kHz	0.17 0.15 0.12	353-373 353-373 353-373	0.19	$5.0x10^{-7}$	0.83	0.76	0.68
P_5	30 kHz 100 kHz 1000 kHz	0.27 0.22 0.16	343-363 343-363 363-373	0.21	$1.0x10^{-7}$	0.89	0.82	0.75
P_6	30 kHz 100 kHz 1000 kHz	0.20 0.18 0.17	353-373 323-343 353-373	0.19	$2.0x10^{-7}$	0.70	0.62	0.55
P_7	30 kHz 100 kHz 1000 kHz	0.23 0.21 0.19	343-373 343-373 353-373	0.42	$2.0x10^{-7}$	0.61	0.57	0.54
P_8	30 kHz 100 kHz 1000 kHz	0.23 0.19 0.17	363-373 353-373 353-373	0.11	$1.3x10^{-6}$	0.89	0.75	0.61
P_9	30 kHz 100 kHz 1000 kHz	0.26 0.24 0.20	343-373 343-373 353-373	0.10	$5.0x10^{-7}$	0.92	0.75	0.60
P_{10}	30 kHz 100 kHz 1000 kHz	0.35 0.25 0.22	353-373 353-373 353-373	0.13	$4.0x10^{-7}$	0.77	0.67	0.57

Table (V-2): Continue.

Samples	F	E_a (eV)	# Temp. Range (K)	W_M (eV)	* σ $ohm^{-1}.cm^{-1}$	$ s At Temp. Range (K)		
						313 K	343 K	373 K
P_{11}	30 kHz 100 kHz 1000 kHz	0.20 0.15 0.13	323-343 353-373 353-373	0.18	$1.0x10^{-7}$	0.83	0.76	0.67
P_{12}	30 kHz 100 kHz 1000 kHz	0.26 0.25 0.14	353-373 353-373 353-373	0.21	$1.0x10^{-7}$	0.67	0.59	0.53

* σ_{AC} at 353 K and frequency of 100 kHz.

Temperature range at which the activation energy, E_a, was calculated.

$ Temperature range at which s value was calculated.

F Frequencies at which the activation energy, E_a, was calculated.