

## Anomalous dielectric dispersion in glycol chitosan—carboxy methyl cellulose polyelectrolyte complex containing alkali ions

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**Abstract.** In films of the polyelectrolyte complexes of glycol chitosan (GC) with alginic acid (AA) and hyaluronic acid (HA) anomalously large dielectric dispersion was observed in the range 1 to 100 kHz above 50°C. This was attributed to the formation of electrical double layers around the polyanion by the sodium ions inevitably present in the films.

To test this hypothesis films of GC with carboxy methyl cellulose were prepared with different concentrations of lithium, sodium and potassium ions. The films were found to absorb much larger amounts of sodium than lithium or potassium. Dielectric measurements from –40 to 80°C in the range 1 to 100 kHz showed anomalously large dispersion above 50°C in films with the higher concentration of alkali ions. The dispersion could be fitted to Schwarz's equations. The characteristics of the fit were similar to those in GC—AA and GC—HA films supporting the hypothesis that the anomalous dispersion is due to an electrical double layer formed around the polyanion by the alkali ions.

**Keywords.** Anomalous dielectric dispersion; polyelectrolyte complex; Schwarz's equation; glycol chitosan

### 1. Introduction

Srinivasan and Kamalam (1982a) studied the temperature dependence of dielectric constant  $\epsilon'$  and loss  $\epsilon''$  from 1 to 100 kHz of thin films of polyelectrolyte complexes of glycol chitosan (GC) with the polyanions dextran sulphate, carboxy methyl cellulose, polygalacturonic acid, and alginic acid. The last named complex exhibited an anomalous behaviour. Above 40°C, the dielectric constant and loss rise very rapidly with temperature. The increase is more rapid at the low frequency end. For example at 2 kHz,  $\epsilon'$  is 10.5 at 35.8°C and 787 at 65.7°C. There is a corresponding increase in loss.

Srinivasan and Pushpa (1983) observed a similar behaviour in the polyelectrolyte complex of GC with the mucopolysaccharide hyaluronic acid (HA).

Schwarz (1962) proposed a model to account for the very large dispersion in the dielectric properties of colloidal suspensions in electrolytes. According to this model fixed charges on the colloidal particle attract microions of opposite charge in the electrolytes. The latter form an electrical double layer around the colloidal particle. When an electric field is applied the mobile microions redistribute themselves in the double layer giving rise to large dipole moments. Assuming the double layers to be spherical having the same radius and carrying a uniform surface density of charge, and supposing a range of relaxation energies to be equally probable, Schwarz derived the following two equations for the incremental dielectric constant  $\Delta\epsilon'(\omega)$  and loss  $\Delta\epsilon''(\omega)$

$$\Delta\epsilon'(\omega) = A \ln \frac{1 + \omega^2\bar{\tau}^2}{\xi_0^2 + \omega^2\bar{\tau}^2}, \quad (1)$$

$$\Delta\epsilon''(\omega) = B \tan^{-1} \frac{(1 - \xi_0)\omega\bar{\tau}}{\xi_0 + \omega^2\bar{\tau}^2}. \quad (2)$$

Here  $\bar{\tau}$  is the relaxation time corresponding to the mean energy  $\bar{E}$  of relaxation.

$$\xi_0 = \exp(-\Delta\bar{E}/kT) \quad (3)$$

where  $\Delta\bar{E}$  is the spread in the relaxation energies and

$$B = 2A. \quad (4)$$

Srinivasan and Kamalam (1982a) postulated that the sodium ions, which would anyway be present in the GC-AA film because the film was prepared from the sodium salt of AA, became mobile as the temperature was raised. These ions could break the electrostatic bonds between the fixed positive and negative charge on the polycation and polyanion respectively and form an electrical double layer around the polyanion. At any given frequency  $\omega$ , these authors found the incremental dielectric constant and loss in the following way. The curves depicting  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  as a function of temperature below 30°C were extrapolated to higher temperatures. The difference between measured values and extrapolated values at a temperature  $T$  gave the incremental values  $\Delta\epsilon'(\omega)$  and  $\Delta\epsilon''(\omega)$ . The incremental dielectric constant and loss as a function of frequency at a given temperature were then fitted to Schwarz's equations (1) and (2). The fit was reasonably good. It was found that (i)  $\bar{\tau}$  was of the order of  $10^{-5}$ – $10^{-4}$  seconds. (ii)  $\xi_0 \simeq 10^{-8}$  indicating that the spread in relaxation energies  $\Delta\bar{E}$  is very wide compared to  $kT$ . (iii)  $\bar{\tau}$  from the fit to  $\Delta\epsilon''$  was nearly five times as large as  $\bar{\tau}$  from the fit to  $\Delta\epsilon'$  and (iv)  $A/B \simeq 0.2$  instead of 0.5. The last two factors might be because the assumptions involved in Schwarz's theory were too simple to be realised in practice.

Srinivasan and Pushpa (1983) also observed anomalous behaviour of  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  above 50°C in the GC-HA complex. Here again the incremental dielectric constant and loss could be fitted to the Schwarz equations. The constants of the fit exhibited the same features as in GC-AA complex.

In order to verify that the anomalous dielectric behaviour is due to the alkali ion, it was decided to check if similar anomalous dielectric behaviour could be induced in GC-carboxy methyl cellulose (CMC) film by the doping of the film with alkali ions. The results of such experiments are reported in this paper.

## 2. Details of preparation of the films

GC (mol. wt 88,000) was obtained from the Sigma Chemical Company, St. Louis, Missouri, USA. Sodium carboxyl methyl cellulose was obtained from the British Drug House. The degree of substitution determined by Srinivasan and Kamalam (1982a) was 0.63. Sitaramiah and Goring (1962) studied the hydrodynamic properties of sodium CMC in aqueous solutions. They found a molecular weight of the order of  $10^5$  when the degree of substitution was in the range of 0.62–0.66.

GC and Na-CMC were separately dissolved in hot distilled water to prepare solutions of concentration 1 mg/ml. A buffer solution of pH 2.6 was prepared. Srinivasan and Kamalam (1982a) had shown that the mixing ratio of the complex was nearly stoichiometric at this pH. GC solution (14 ml) was taken and 120 ml of buffer solution was added to this and mixed well. Na CMC solution (63 ml) was then added. The complex was allowed to precipitate slowly on mercury for 24 h. The supernatant liquid was then siphoned off and the precipitate washed with deionised water several times

and dried at 40°C under reduced pressure. Transparent films of uniform thickness between 15 and 60 $\mu$  were obtained.

Initially the films were dipped for several hours in 1 M NaBr solution. The films were then removed, washed with distilled water and dried. The dielectric constant was then measured at 1 kHz at 80°C to find if the film exhibited an anomalously large value. It was observed that a film dipped for 8 h in NaBr showed a value of  $\epsilon'$  (1 kHz) = 6.58 while a film dipped for 44 h showed  $\epsilon'$  (1 kHz) = 6.44 at the same temperature. This showed that the dielectric properties of the film were not significantly affected by dipping them in NaBr probably because Na did not get into the film once the complex was formed.

It was then decided to add the salt solution even while mixing the polycation polyanion solutions. Salt solution of alkalichloride (0.1 ml) of different molarity was added to the mixture of GC and buffer solutions before the CMC solution was added. Films were then obtained which showed anomalously large dielectric constants at high temperatures.

Three films each were prepared with the addition of lithium chloride, sodium chloride and potassium chloride. The quantity of the alkali ion in the film was varied by changing the molarity or quantity of salt solution added. After the measurements each film was dissolved in concentrated nitric acid and the solution made up to 10 ml. The content of the alkali ion per ml of the solution was determined by atomic absorption spectroscopy. Potassium content was measured at the Regional Sophisticated Instrumentation Centre of IIT, Madras, while lithium and sodium contents were measured at the Radio Chemistry Laboratory of the Reactor Research Centre, Kalpakkam. From the weight of the dissolved film, one may estimate the weight of the alkali ion per gram of the film. Table 1 lists the alkali metal content in the films prepared. It is obvious that the PEC film of GC-CMC takes sodium preferentially as compared to lithium and potassium. While the maximum concentration of lithium and potassium is 360 and 594  $\mu\text{g/g}$  of the complex respectively, the maximum concentration of sodium is 24,500  $\mu\text{g/g}$ . The films prepared with the addition of salt solution were found to absorb moisture on exposure to air while films prepared without the addition of salt did not appear to do so.

Table 1. Estimation of alkali metal concentration in films of GC-CMC by atomic absorption

Code No. of the film	Molarity of salt solution (M)	Volume (ml) of salt solution added	Weight of the film W (g)	Alkali metal conc. ( $\mu\text{g/ml}$ )	Weight of metal per g of complex ( $\mu\text{g/g}$ )
Li-I	0.1	0.1	0.0222	< 0.1	< 45
Li-II	1.0	0.1	0.0283	0.3	106
Li-III	1.0	0.3	0.0278	1.0	360
Na-I	0.01	0.1	0.0230	14.0	6087
Na-II	0.1	0.1	0.0200	21.0	10500
Na-III	1.0	0.1	0.0396	97.0	24500
K-I	0.01	0.1	0.0393	0.65	162
K-II	0.1	0.1	0.0220	0.47	214
K-III	1.0	0.1	0.0399	2.37	594

### 3. Dielectric measurements and analysis of results

The dielectric constant  $\epsilon'$  and loss  $\epsilon''$  of the films were measured in the range 1–100 kHz using a GR 1615 A capacitance bridge. The experimental arrangement to cover the temperature range from  $-40^\circ$  to  $80^\circ\text{C}$  has been described by Kamalam (1981). It should be mentioned that the accuracy in the absolute  $\epsilon'$  value is only 10% but the relative  $\epsilon'$  values at different frequencies and different temperatures are much more accurate on one and the same film as the errors in the geometrical parameters associated with the capacitance drop out.

Of the nine films prepared, K II and K III could not be measured because of the unavailability of the capacitance bridge.

In order to save space, we show in figures 1a, b to 4a, b the  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  values as a function of frequency at different temperatures for Na-I, Na-III, Li-III, and K-I.

It is well known that the configuration of the polyions in solution will depend on the ionic strength of the solution. Hence the structure of the complex will also depend on the ionic strength. At very low temperatures the dielectric constants of the various films are not exactly the same (as shown in table 2). However, these experiments were aimed at finding out if an anomalous dielectric behaviour similar to that observed in GC-AA film can be induced in GC-CMC film by introducing alkali ions in the film. Figures 1 to 4 clearly indicate that such is the case. For example if we consider the three films Na-I, Na-II, and Na-III,  $\epsilon'$  at 1 kHz is 14.9 at  $76^\circ\text{C}$  in Na-I, 132.9 at  $77.2^\circ\text{C}$  in Na II and 284.6 at  $82.2^\circ\text{C}$  in Na-III. In the case of lithium-doped samples  $\epsilon'$  at 1 kHz increases from 17 at  $75.7^\circ\text{C}$  in Li-I, to 86.9 at  $75.9^\circ\text{C}$  in Li-III. Though K-II and K-III could not be measured over the entire temperature range a similar trend was observed in potassium-

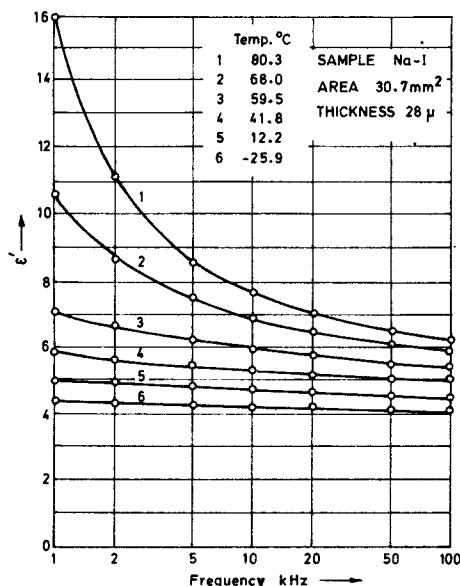


Figure 1a. Variation of  $\epsilon'$  in sample Na-I as a function of frequency at different temperatures.

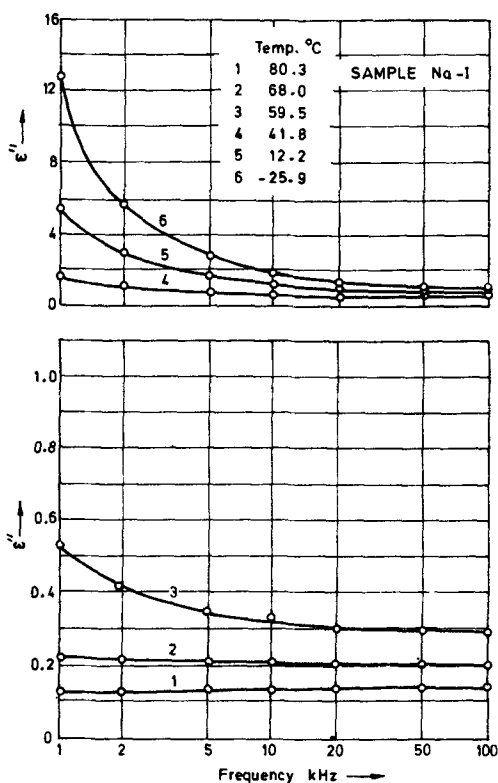


Figure 1b. Variation of  $\epsilon''$  in sample Na-I as a function of frequency at different temperatures.

doped films also. For example,  $\epsilon'$  at 1 kHz was found to be 13 at 69.3°C in K-I, 19.5 at 74°C in K-II and 31 at 69.7°C in K-III.

The incremental dielectric constants  $\Delta\epsilon'(\omega)$  and  $\Delta\epsilon''(\omega)$  were calculated at two or three highest temperatures of measurement for Li-II, Li-III, Na-II, Na-III and K-I films following the procedure used by Srinivasan and Kamalam (1982a) in GC-AA films. These values were fitted to the Schwarz equations (1) and (2). Table 3 shows the degree of fit obtained in Na-III film. Similar fits were obtained in other films.

The parameters needed to fit  $\Delta\epsilon'(\omega)$  and  $\Delta\epsilon''(\omega)$  in the five films Na-II, Na-III, Li-II, Li-III and K-I at different temperatures are collected in table 4. For comparison the parameters used for GC-AA film by Srinivasan and Kamalam (1982a) and for GC-HA film by Srinivasan and Pushpa (1983) are also shown. It is apparent that in the alkali doped GC-CMC films also (a) the  $\bar{\tau}$  values needed to fit  $\Delta\epsilon'$  are of the order of 10–20  $\mu\text{s}$  while  $\bar{\tau}$  values needed to fit  $\Delta\epsilon''$  data are between 60–250  $\mu\text{s}$ . (b)  $\zeta_0 \approx 0$  indicating a large spread in the relaxation energies. (c)  $A/B$  value is also in the range of 0.05 to 0.2. (d) While  $A$  and  $B$  generally increase with increase in salt concentration they are not proportional to the salt concentration.

The behaviour of Li-III sample is significantly different from the others. At 75.9°C,  $A$  is nearly twice as large as  $B$ . Also the dielectric loss  $\epsilon''$  exhibits a peak between 5 and 10 kHz. Such a peak is not observed in other specimens.

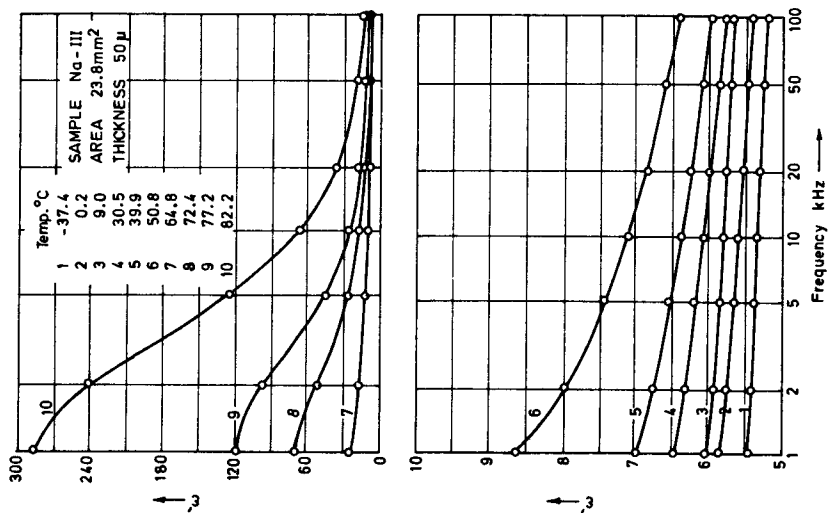


Figure 2a. Variation of  $\epsilon'$  in sample Na-III with frequency at different temperatures

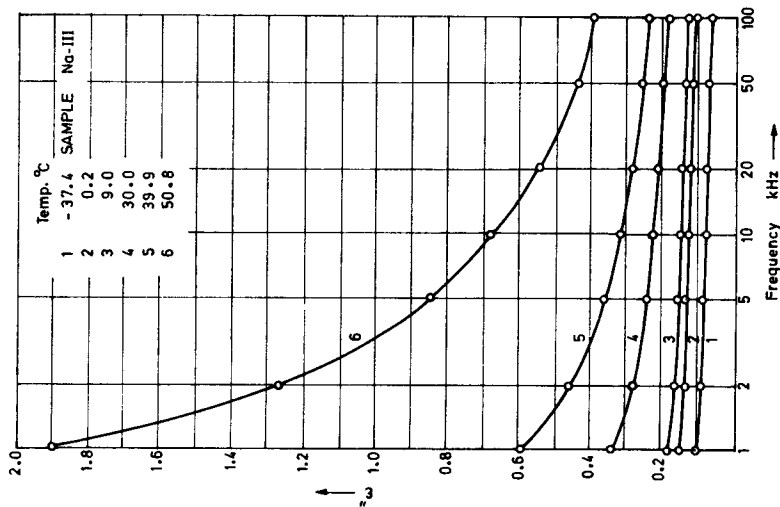


Figure 2b. (i) Variation of  $\epsilon''$  in sample Na-III with frequency at different temperatures

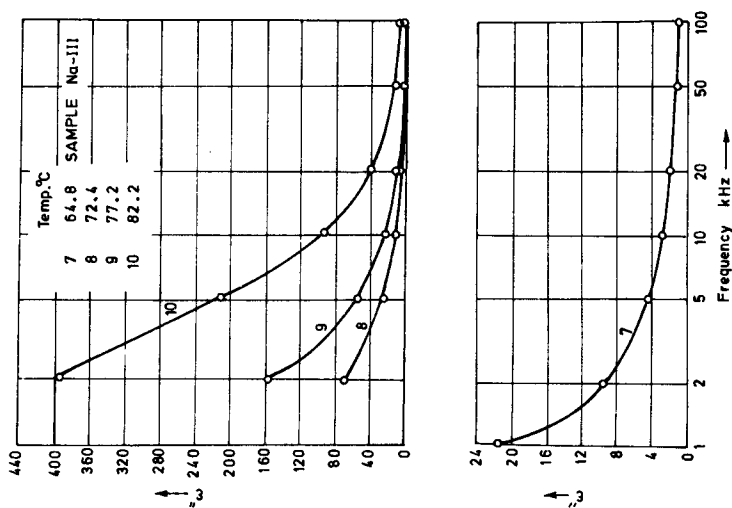


Figure 2b. (ii) Variation of  $\epsilon''$  in Na-III sample with frequency at different temperatures

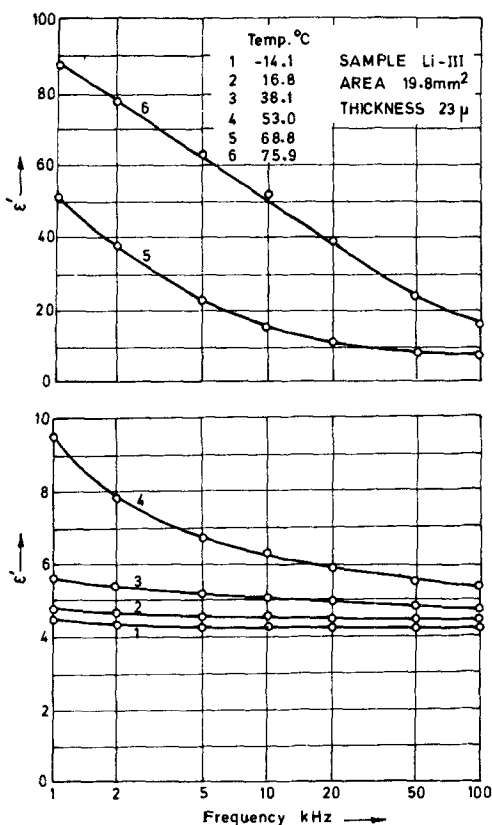


Figure 3a. Variation of  $\epsilon'$  in Li-III sample with frequency at different temperatures

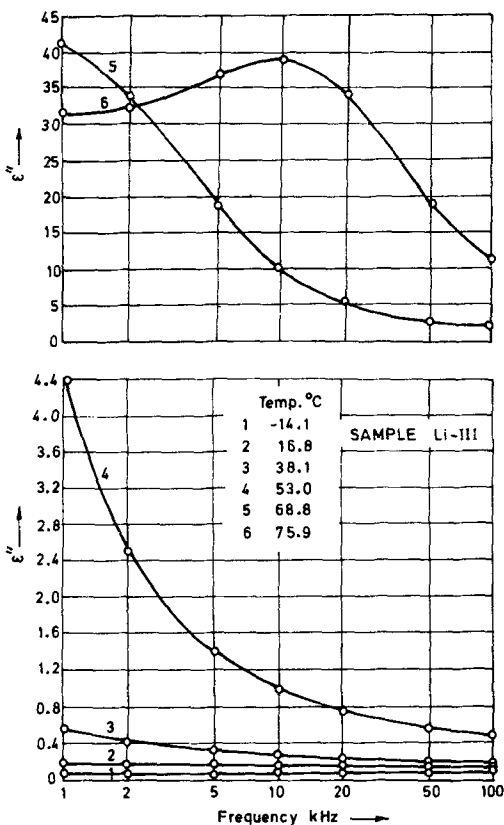


Figure 3b. Variation of  $\epsilon''$  in Li-III sample with frequency at different temperatures

The features (a), (b) and (c) of the fit to the dielectric properties observed in the films of GC-CMC to which a salt is deliberately added during preparation are similar to the features of the fit to  $\Delta\epsilon'(\omega)$  and  $\Delta\epsilon''(\omega)$  in GC-AA films first observed by Srinivasan and Kamalam (1982a). In GC-AA film, and in GC-HA film studied later by Srinivasan and Pushpa (1983), no salt was added during preparation. The similarity in behaviour appears to support the surmise that in GC-AA and GC-HA films the unusual dielectric properties arise because microions form electrical double layers around fixed charges on the polyanions and at high temperatures these double layers make a large contribution to the dielectric constant and loss.

#### 4. Electrical conductivity

To see whether the large change in dielectric properties of the films by the incorporation of alkali ions is also accompanied by drastic changes in electrical conductivity, the current through these films at a fixed DC voltage of 20 V was studied as a function of temperature. In figure 5, the current normalised to the value  $I_0$  at 30°C is plotted as a function of the reciprocal of the absolute temperature for Na doped samples. The

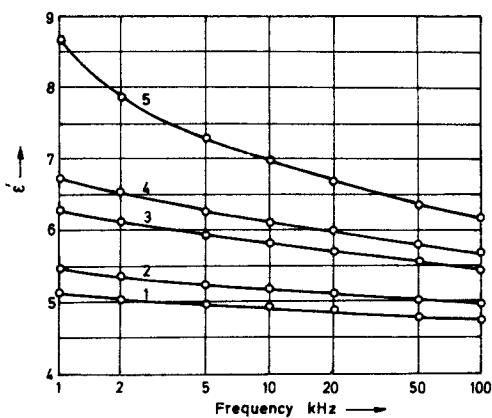
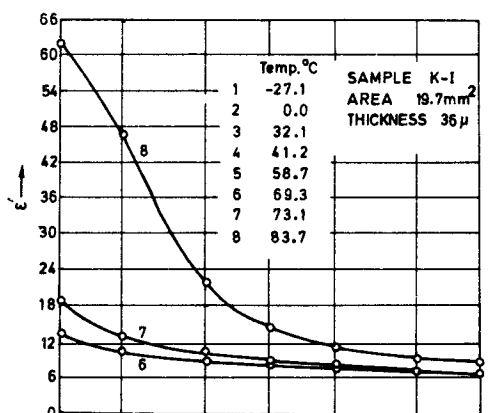


Figure 4a. Variation of  $\epsilon'$  in sample K-I with frequency at different temperatures

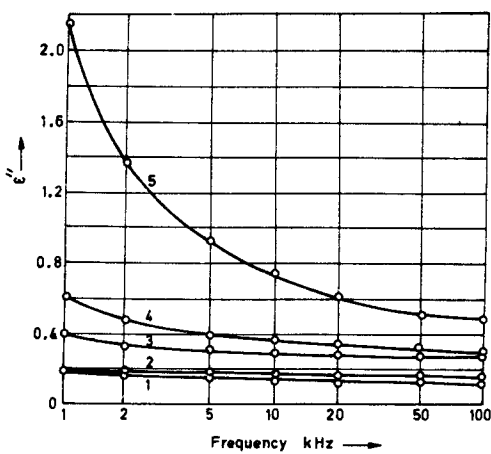
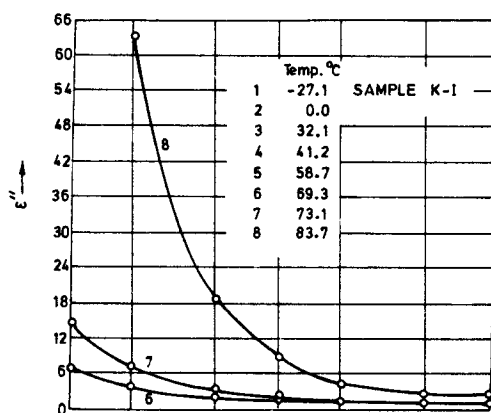


Figure 4b. Variation of  $\epsilon''$  in sample K-I with frequency at different temperatures

Table 2. Dielectric constant values at low temperatures of various films of GC-CMC with alkali ions

Sample	Temp (°C)	$\epsilon'$	
		100 kHz	1 kHz
Li-I	-6.65	5.59	6.24
Li-II	-10.1	3.31	3.54
Li-III	-14.1	4.16	4.40
N-I	-25.9	4.04	4.41
Na-II	-24.0	4.05	4.30
Na-III	-37.4	5.20	5.46
K-I	-27.1	4.72	5.09
K-II	-20.2	3.43	3.71
K-III	-26.5	4.77	5.06
Without salt	-17.0	4.01	4.33



Table 3. Fit to incremental dielectric constant and incremental loss in Na-III film using Schwartz equations

Temp (°C)	Frequency (kHz)	Fit to $\Delta\epsilon'(\omega)$				Fit to $\Delta\epsilon''(\omega)$				Standard deviation $\sigma$		
		Parameters A	Parameters $\xi_0$	$\bar{\tau}/\mu\text{s}$	$\Delta\epsilon'(\omega)$ calc.	$\Delta\epsilon'(\omega)$ obs.	Standard deviation $\sigma$	Parameters B	Parameters $\xi_0$		$\bar{\tau}(\mu\text{s})$	$\Delta\epsilon''(\omega)$ calc.
82.2	1				282	278						
	2				209	232				380	395	
	5				118	119				194	210	
	10	52.6	0	11.0	59.5	59	10.3	387	0	65.9	90	11.4
	20				22.2	31					50.6	40.4
77.2	50				4.2	13.7				20.9	14.1	
	100				1.1	8.4				10.4	7.7	
	1				115	112.7						
	2				82	90.0				145	155	
	5				41.7	37.0				60	52	
72.4	10	24.1	0	14.8	18.5	19.4	4.6	422	0	223	23	5.7
	20				6.1	10.8				15	10.6	
	50				1.1	5.8				5.9	4.9	
	100				0.3	4.1				3.0	3.1	
	1				61.0	61.3						
72.4	2				42.2	44.8				62.7	66.7	
	5				19.7	18.8				25.7	22.2	
	10	14.0	0	18.1	8.0	10.7	2.7	197	0	243	10.9	2.38
	20				2.5	6.6				6.5	5.7	
	50				0.43	3.9				2.6	3.0	
100				0.11	3.0				1.3	2.0		

**Table 4.** Parameters required to fit the dispersion of incremental dielectric constant and loss in alkali doped GC-CMC films.

Sample	Temp (°C)	Parameters in fitting $\epsilon'$		Parameters in fitting $\epsilon''$	
		A	$\bar{\tau}(\mu\text{s})$	B	$\bar{\tau}(\mu\text{s})$
Li-II	77.7	13.3	15.4	270	250
	74.2	3.9	11.0	51.0	250
Li-III	75.9	8.27	1.07	33.0	6.7
	68.8	5.43	4.14	35.7	54.8
Na-II	77.2	29.1	13.6	214	99.0
	63.8	2.73	10.4	29.5	227
Na-III	82.2	52.6	11.0	387	65.9
	77.2	24.1	14.8	422	223.0
	72.4	14.0	18.1	197	243.0
K-I	83.7	12.3	17.2	48.9	81.0
GC-HA	82.9	7.66	4.2	37.2	37.3
	72.9	2.99	4.1	14.4	62.4
GC-AA	65.7	123.2	3.8	680.4	17.0
	58.7	70.9	4.9	352.5	21.4

curves for Li and potassium-doped samples are similar. For comparison in each of these figures the normalised current *vs* reciprocal of the absolute temperature of the GC-CMC film (without the addition of salt) measured by Srinivasan and Kamalam (1982b) is plotted.

Table 5 gives the conductivity  $\sigma$  of the film calculated from the dimensions of the coated electrodes and the current. The conductivity values are given at 0 and 70°C. The normalising current  $I_0$  is also indicated. While the conductivity of lithium, sodium and potassium doped specimens at 70°C increases with concentration, Li-III and K-II samples are exceptional in their behaviour. It has already been noted that the dielectric behaviour of Li-III was different from the rest of the sample. It is noteworthy that the increase in conductivity in the other samples is not proportional to the concentration of the alkali ion.

The absorption of phenomenally large amounts of sodium has not increased the conductivity proportionately. Michels *et al* (1965) found a similar result when they incorporated sodium in large amounts by dipping a film of the PEC formed by combining polystyrene sulphonate with polyvinyl benzyl trimethyl ammonium chloride. While phenomenally high values of dielectric constant were observed in the doped films, the change in conductivity was small. This shows that a large percentage of sodium ions are not free to transport charge; however, they contribute to the dielectric constant. From figure 5, it can be seen that the addition of ions causes an increase in activation energy for conduction as is evident from the increase in slope.

## 5. Conclusion

The anomalous dielectric behaviour induced in GC-CMC films by the incorporation of

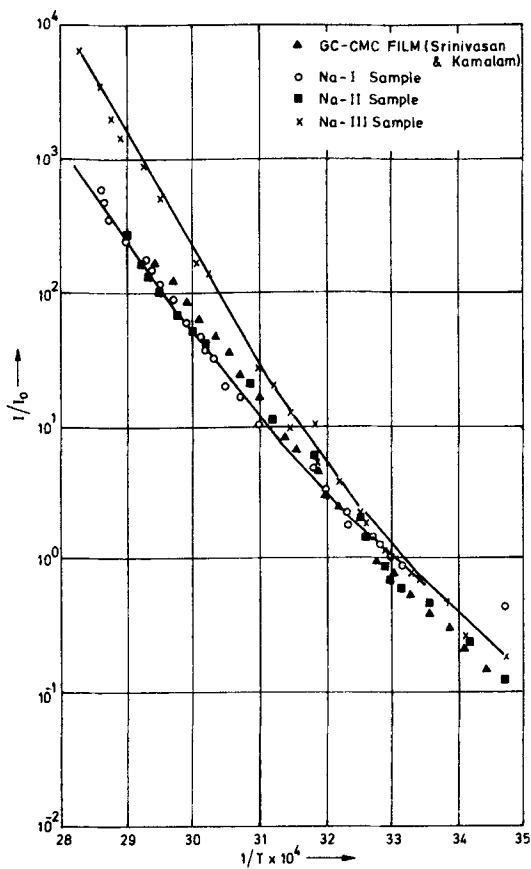


Figure 5. Normalised current vs reciprocal of absolute temperature for Na doped GC-CMC films

Table 5. Conductivity data at 0 and 70°C for GC-CMC films doped with alkali ions

Sample	$\sigma_0 \times 10^{14}$ (mho/cm)	$\sigma_{10} \times 10^{11}$ (mho/cm)
Li-I	11	16
Li-II	2	108
Li-III	3	29
Na-I	12	32
Na-II	5	79
Na-III	8	374
K-I	14	116
K-II	9	86
K-III	18	203

alkali ions supports the hypothesis of Srinivasan and Kamalam (1982) that the anomalous behaviour observed in GC-AA film is due to the formation of an electrical double layer around the polyanion by the sodium ions.

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