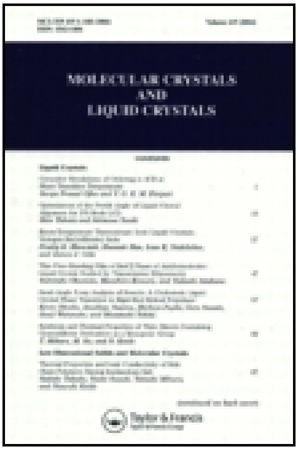

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On the Dynamics of Space Charge Regions in Organic Materials

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On the Dynamics of Space Charge Regions in Organic Materials

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Electrical conductivity phenomena has been studied in cyano-alkylbiphenyl materials as well as noncrosslinked epoxide adhesives. Measurements were done under DC as well as AC voltage excitation. These were comprising frequency range $10^{-5} \div 10^{4}$ Hz or equivalent time interval and were carried for low voltage signals. Blocking electrodes were used and thick samples. It is assumed that sample response observed in indicated above frequency region is due heterocharge formation at the interface. Sample dielectric response observed in this case is assumed to be due to heterocharge formation. It may be observed at DC voltage excitation, mainly. The response is similar to that produced by so called CPA element.

Keywords: space charge; ionic conduction; polar dielectric materials; low frequency dispersion

INTRODUCTION

It is known elsewhere, that liquidcrystalline materials, cyano - alkylbiphenyl materials particularly , supplied with ITO(indium - tin oxide) or metal electrodes are exhibiting DC like electrical conductivity. On other hand when studied under small voltage AC excitation these are exhibiting strong electrode polarisation phenomena. Our investigations [1,2] are indicating coexistence of these two properties. According to our suggestions theseare related to formation of space charge regions in vicinity of electrodes. Possibility of space charge formation is very well known phenomenon and subject of electrochemical research. In majority of cases at interfacial regions charge recombination take place through channels of chemical reactions. It is our suggestion that in the case of materials in test recombination process is strongly depressed and its influence in the time window of experiment is negligible. The lack of recombination is the cause of strong electrode field. Thus carrier emission from an electrode take place [3,4]. Injected carriers attached to host molecules are the source of DC conductivity. The phenomenon is observed at least in nematic, smectic A and isotropic phases. The phase change is influencing the value of carrier mobility, only. The anisotropy of the conductivity one may record as well as in the case where conductivity is due to bulk impurity ions itself or in the case of conductivity due to the electrode effect is because of to mobility anisotropy.

EXPERIMENTAL

For «Time Domain» measurements [5] «sandwich» type samples were used with thickness 200 μm, mainly. Beside indium - tin oxide (ITO), Cu and Au metal electrodes were used. Voltage window of measurements was 0.1V-10V, time window $10^{-4} \div 10^{4}$ s, current window $10^{-3} \div 10^{-13}$ A. The average electric field strength was less than 5kV/m. In the case of «Frequency Domain» measurements [6] FRA (Frequency Range Analyser) records were performed. The thickness of the samples was ranging from 100 μm to 200μm, AC voltage applied to the sample 0.1 V rms. FRA system was covering frequency range 10^{-5} - 10^{5}Hz. The measurements carried under DC bias were also performed. In case of step voltage records, Fourier transforms of the data were done for better comparison. The range of frequency obtained was in this case 10^{-4} - 10^{3} Hz. However at high frequency end a distortion of the results of the transform was observed frequently. Experiments were carried not only in cyano - alkylbiphenyl materials but also in noncrosslinked epoxide materials such as Epicote 828 [7], Epidian 3, and Epidian 6 [8]. In case of cyano-alkylbiphenyl materials numerous results are for 5CB where reliable values of ionic mobility are existing.

It may be anticipated, that small signal case one can obtain where chemical relaxation time is shorter than ionic time of transit. However the estimation of these values is not always possible because of the lack of reliable data concerning carrier mobility, dissociation and recombination rates. However there is another possibility. According to Ross Macdonald statement [9], when external DC bias is not influencing the value of AC conductivity charge equilibrium and local charge neutrality is present. Such experiments were done for numerous cases for electrical DC bias of the order of 10 V. In any case there was change recorded in the value of AC conductance [2,10,11]. So, the consideration of the space charge concept seems to be justified.

The response of the sample of 5CB

In time domain the response of 5CB sample is like that shown in Fig.1. There are the following properties of the response [1,2,3,4,10,11]. The response is linear except the region of elevated time where DC(called electrode current) conductance is observed. For low voltage the above conductivity is negligible. Discharge current is mirror one of charging current(subtracted of electrode current). Electrode current is superlinear function of the voltage applied to the sample.

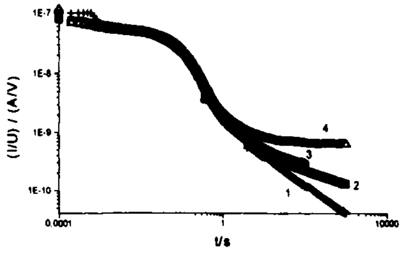

FIGURE.1. Response of the sample ITO/5CB/ITO recorded at 300,5 K, thickness 0.2mm,1 - discharging current at voltage U = 0.1V, 2 -charging current at U = 0.1V, 3-charging current at U = 1V, 4-charging current at voltage U = 10V, I-electrical current, U - voltage applied.

The characteristic features of the response shown in log - log representation in Fig.1 are as following. For short time the response is due to transport and other processes taking part in the bulk of material.

The onset of electrode processes represents a kink on the plot. Than the plot in log - log representation is following, approximately the line with the slope index – n till the onset of electrode current. It is assumed that the portion of the slope with index – n is related to space charge evolution in time. In reality the plot may be fitted by more complicated functions as it was indicated before [2,3,4]. The model proposed by W.L.Szymański [4,12,13] yields the onset of electrode polarisation depending on carrier mobility and carrier concentration. The increase of ionic mobility due rise of temperature may shift the onset to shorter time. The same effect is due to increase of the density of carriers. Most of the data regarding dielectric response of materials are in frequency representation [14]. Thus the data collected in time domain were transformed to frequency domain for better comparison with that obtained due to AC voltage excitation. For the representation of the data of interest capacitance C' and C'' vs. frequency f plots will be shown in log - log representation in Fig. 2.

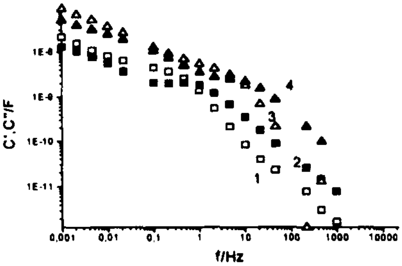

FIGURE.2. The C' and C'' plots for different temperature, sample Cu/5CB/Cu,(area 0.25 cm^2, thickness 0.2mm). Fourier transforms of discharge response. 1 - C' at 297K, 2 -C'' at 297K, 3 - C' at 333K, 4 - C'' at 333K.

Interesting feature of above response is pseudo-parallel behaviour, of the log - log plot of C' and C''. Such behaviour is the reason of small variations of tan δ value, for the range of frequency $f < f_s$, where heterocharge is influencing current flow. It is worth to notice that the index of the slope of C', C'' plots is close to 0.4 and in the limit of error seem to be temperature independent. The value 0.4 is correlated with 0.6 observed in the case of recording of log of current vs. log of time plots. As was stated before [5] for the case of liquidcrystalline materials, in the records collected by means of AC voltage excitation, in comparable window of frequency no such response was observed. For verification of this assumption it was worth to check another materials. . In our case these were noncrosslinked epoxide materials.

Epoxide materials

The epoxide materials were studied under DC and AC voltage excitation. The thickness of the samples was 200μm, for electrode materials metallic Au and Cu was used. In respect to the records described above, the range of sample electrical linearity was smaller and a marked differences between Au and Cu electrodes were observed. In case of Au electrodes DC like conductivity was recorded. On other hand in the case of Cu electrode a decay of the current in long time limit was observed. However the index of the slope of the log of current I vs. log of time t was not 0.5 as one may expect(Wartburg impedance) but smaller, around 0.2. The example of AC voltage driven records for epoxide materials are exhibited in Fig.3., where response of the sample Au/Epicote 828/Au is shown. On can see the from the plot change of the slope of C'' plot in low frequency region. The slope n_F changes from 0.98 to 0.64. The first part of the plot with slope 0.98 is commonly interpreted [14] as related to „quasi-DC» conductivity of the material. The slope n_F equal to 0.64 have to be linked to any other mechanism, space charge response, par example.

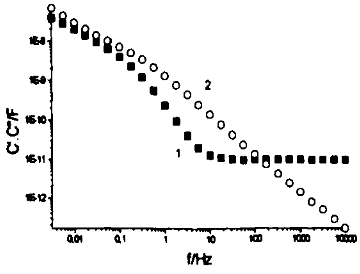

FIGURE.3. FRA record for sample Au/Epicote 828/Au at 333K under excitation of 0.1V rms. 1-C', 2-C''.

For comparison is shown in Fig.4 a record obtained due to Time Domain measurement. There is, as in the case of Fig.3. a kink on lgC'' vs. log f plot at comparable frequency value. However the slopes of AC e and DC voltage run records are different. On contrary, in the case of Cu electrode the agreement between the data recorded either in time domain or in frequency domain is much closer. This is assumed due to increased importance of interfacial recombination process [10, 15].

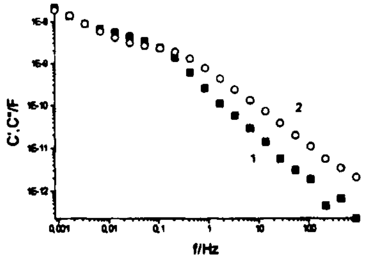

FIGURE.4. Fourier transform of the Time Domain record for sample Au/Epicote 828/Au at 333K 1-C', 2-C''.

INTERPRETATION

In more early publications related to water-based electrolytes and solid ionically conducting materials double layer was assumed to be in stationary condition [16], and described by Debye-like response function [17]. Thus, in equivalent circuit series or parallel RC connections was proposed. Latter it has been found that the other kinds of response are present. These were CPA (Constant Phase Angle), „real capacitor» or, due to A.K. Jonscher, low frequency dielectric dispersion functions. The basic feature of these concepts is that C'/C'' = cot δ = cons. Numerous situations are cited [14] where such behaviour has been detected . In our case, for small signal sample excitation direct current is virtually absent, and frequency range of C''/C' ≈ cons is considerable, as shown in the Fig 2. One may try to explain this finding by means of fractal properties of the surface of electrode. However, in our experiments different electrodes were used in relation to the material or to the method of its deposition. In all the cases similar relations were observed. It will be quite unexpected if all these surfaces were exhibiting similar fractal properties. In papers of Hill and Dissado [18] fractal nature of the medium for account of fractal results was suggested. The change of phase, as in the case of liquid crystalline materials or viscosity in the case of epoxide materials is not supporting of such concept. Thus we conclude, that it is quite probable that the heterocharge formation is responsible for observed effects.

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