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ELECTROPHYSICAL PROPERTIES OF THE DIAZONIUM SALT SOLUTIONS IN THE SOLID POLYMERIC MATRIXES

*P.O. Kondratenko*¹, *Yu.M. Lopatkin*², *T.N. Sakun*¹

¹ National Aviation University,
1, Cosmonaut Komarov prosp., 03680, Kyiv, Ukraine
E-mail: pkondrat@ukr.net

² Sumy State University,
2, Rimsky-Korsakov Str., 40007, Sumy, Ukraine
E-mail: yu.lopatkin@meta.ua

Complex of experimental and theoretical researches of electrophysical properties of the solid solutions of diazonium salts (tetrafluoroborat paradietilaminophenyl-diazonium (DEAPhD) and paramethoxyphenyldiazonium (MPhD)) in polymeric matrixes (polyvinyl alcohol, polyvinylpirrolidon, polyvinyletilal and polyvinylacetate) allowed to show that the photocurrent, conditioned by holes, is generated in a matrix under excitation of diazonium salt (DS). Average quantities of the hole mobility in a matrix depending on the DS concentration are found. The energy structure of DS and polymeric matrixes, which explains difference in the generation processes of the current carriers with DEAPhD and MPhD participation, is calculated. It is shown that the ionic conductivity as well as the hole one occurs in polymeric layers.

Keywords: ELECTROPHYSICAL PROPERTIES, PHOTOGENERATION, ENERGY STRUCTURE, SALTS OF DIAZONIUM, POLYMERIC SOLUTIONS.

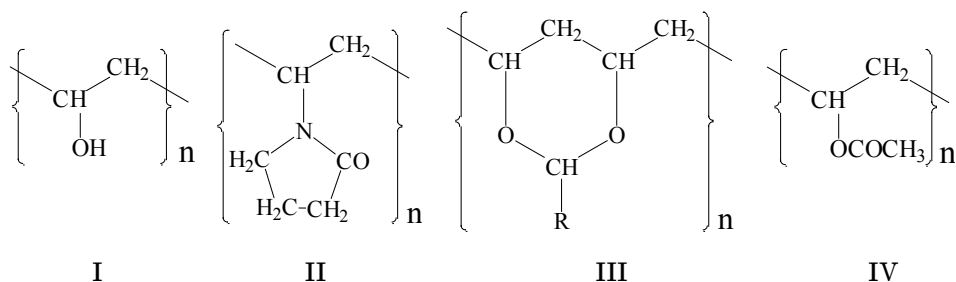
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1. INTRODUCTION

Development of physical methods of information recording has stimulated investigation of physical and photochemical processes in photosensitive layers containing both the binding polymer and the photosensitive component. For clarifying the nature of original processes in such layers the necessity of their photoelectric properties examination has occurred. However, it became clear that the majority of photosensitive components are capable to provide reaction of electron transport from photosensitive component into matrix and inversely. And only the diazonium salts (DS) (photosensitive components of diazotype matter [1, 2]) provide one-sided process – from matrix into diazonium cation [3-5]. That is why in the present work we describe photoelectric properties of the system polymer/DS. Polyvinyl alcohol (PVAL) (I), polyvinylpirrolidon (PVP) (II), polyvinyletilal (PVE) (III) and polyvinylacetate (PVAc) (IV) were investigated as a binding polymer.

As a diazocomponent the tetrafluoroborats of paradietilaminophenil-diazonium (DEAPhD) and the parametoksiphenildiazonium (MPhD) were used. They were injected into polymeric layer, obtained by drying of the 5% polymeric solution and certain DS concentration in the mixture ethanol: acetone (1:1) on quartz substrates at the room temperature during 10 minutes, and then at 353 K during 30 minutes. The thickness of layers was 5-7 μm .

Water-bidistillate was used as a solvent for preparation the layers with PVAL. Water was heated up to 80 °C for obtaining the PVAL solution.



2. EXPERIMENTAL AND THEORETICAL INVESTIGATION METHODS

Laboratory facility for the photoelectric properties investigation consists of lighting unit (the mercury lamp DRSh-250 with the set of color filters: ZhS-18, BS-8, UPhS-1), power supply device (100 V battery), voltage control elements, voltage measuring instrument (digital voltmeter VK2-20) and electrometric amplifier VK2-16. From the amplifier output a signal arrived to the vertical input of XY-recorder LKD4-003. Its horizontal channel was sweeping linearly with the time.

The thin film sample was placed between two clear electrodes (SnO_2 layers on a quartz substrate) into measuring box, plugged into electrometric amplifier input. Studying the photoelectromotive force (photoEMF) the supplemental Teflon layer of 2 μm thickness was placed between the electrode and the sample.

It is necessary to remind, that producing the polymeric layers from solution on a horizontal quartz surface they were found to be non-uniform in thickness: layers are denser near substrate and more distended on a free surface [16]. That is why we can find only averaged parameters, which characterize the photoconduction of polymeric layers.

For theoretical description of experimental study the methods of formal kinetics of photoprocesses in layers were applied, and the quantum-chemical methods (in particular, method of molecular dynamics MM+, based on method MM2 [6], semi-empirical methods MNDO/d and AM1 [7, 8]) were used as well.

3. QUANTUM-CHEMICAL STUDY

For clearing-up the electron transport mechanism in matrix-DS system we have calculated the energy in such a system without electron transport, with transport from matrix into DS and inversely, calculations of DS energy structure in non-dissociated and dissociated states, electron excitation spectrum, and possibility of an electron dark current in matrix-photoproduct system (the photoproduct was obtained by dissociation of the diazonium cation) was estimated as well. The results of calculation are presented in Table 1 and Table 2.

Energy data of Table 2, necessary for charge transport (ChT), ignores the Coulomb interaction between charges after ChT process. After ChT the system geometric structure is non-optimized. Optimization considerably decreases system energy. We have to note, that value of this decreasing exceeds the Coulomb interaction energy between charges after ChT. So, the geometric optimization of molecular system promotes the hole removal and photocurrent or photoEMF arising. As a result, we observe the hole photoconduction in matrix.

Table 1 - Ionization potentials (I_G) and electron affinity energies (E_A) of matrix and DS molecules (in round brackets – in excited state)

Molecule	I_G , eV	E_A , eV
PVE	10,44	-3,03
PVP	8,72	-3,54
PVAc	10,93	-0,61
PVAI	10,67	-2,59
MPhD BF ₄	10,48	3,15
DEAPhD BF ₄	9,30	2,88
MPhD	12,97	6,65 (10,61)
DEAPhD	12,04	6,26 (9,52)

Table 2 – Required energy for electron transport from matrix (M) into DS and from DS into matrix

CT into DS	CT into M	condition	E_{opt}	
7,30	13,51	kk		PVE + MPhD BF ₄
4,19	10,85	opt	3,11	
7,55	12,32	kk		PVE + DEAPhD BF ₄
4,43	9,81	opt	3,12	
5,73	13,99	kk		PVP + MPhD BF ₄
3,97	10,22	opt	1,76	
5,32	12,84	kk		PVP + DEAPhD BF ₄
4,24	9,22	opt	1,77	
7,78	11,09	kk		PVAc + MPhD BF ₄
4,35	9,95	opt	3,44	
8,04	9,91	kk		PVAc + DEAPhD BF ₄
4,60	8,92	opt	3,45	
<i>Note. kk – charge transport without molecular geometry changing (Kramers-Kronig), opt – after geometry optimization</i>				

The position of the MPhD long-wavelength absorption band is 3,96 eV, and of the DEAPhD is 3,26 eV. According to the Table 2 data the generation in PVE occurs at $E > 4,19$ eV (MPhD) and $E > 4,43$ eV (DEAPhD). Similarly in the PVA – 4,35 and 4,60 eV, in the PVP – 3,96 and 4,20 eV.

Thus, MPhD using provides the photoconduction in PVP with excitation into long-wavelength absorption band. In other polymers or using DEAPhD an excitation in higher states is necessary.

DS photolysis results in formation of the aryl cation. It is important to know, if processes with participation of these cations can initiate the photoconduction phenomena. That is why we calculated the energy balance for different transformations of the aryl cation. It was found that in the dark

methoxyphenil cations can capture an electron from matrix, that initiates the hole conduction. At the same time dietilaminophenil cations cannot capture electrons (the barrier value is in the range of 1,2-1,6 eV). Calculations showed that both types of aryl cations can pull out the hydrogen atom from macromolecule. In addition both aryl cations easily react with the anion BF_4^- , and therefore two neutral molecules are formed. Thus, this reaction does not influence on the photoconduction. But it was found out, that in the presence of water vapour the phenols and the acid $\text{H}^+ \text{BF}_4^-$ can be formed, and this acid in water vapour medium ($\text{H}_2\text{O} + \text{H}^+ \text{BF}_4^- \rightarrow \text{H}_3\text{O}^+ + \text{BF}_4^-$) can influence on the slow component of photoconduction.

4. EXPERIMENTAL STUDY AND DISCUSSION OF RESULTS

Photocurrent kinetics under excitation switching on/switching off for different DS concentrations in the PVAI matrix is presented in Fig. 1. As seen from Fig. 1, the current growth stops after certain time τ . So, it is possible to assume, that all carriers reached the opposite electrode and the dynamic equilibrium is attained.

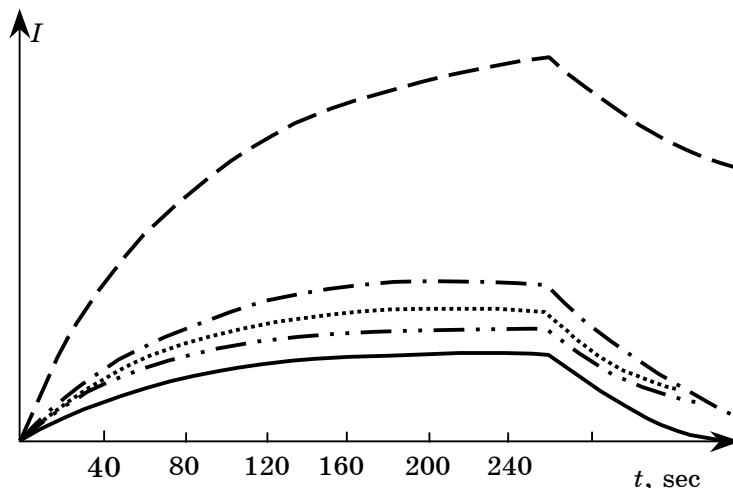


Fig. 1 – Photocurrent kinetics under excitation switching on/switching off for different DS concentrations in the PVAI matrix: pure PVAI (---); DEAPhD, 10^{-3} M (- . . -); MPhD, 10^{-3} M (.....); DEAPhD, 10^{-2} M (- - -); MPhD, 10^{-2} M (- - -)

Using data of the polymeric layer photoconduction we calculated average quantities of the light-generated current carrier concentration n versus the concentration of DS molecules (see Fig. 2).

These quantities show that DS injection into PVAI and PVP increases the concentration n and decreases the last one into PVE. As to PVAc matrix, its reaction to MPhD and DEAPhD injection is diametrically opposite: DEAPhD increases n value and MPhD decreases it.

The reason of that could be defects or uncontrollable impurities, which provide the necessary conduction. Adding the small DS concentrations the defects removal is possible and as a consequence the photocurrent reducing. Also we see that the concentration of photogenerated current carriers for layers with MPhD is larger than for layers with DEAPhD in all polymeric matrixes except of PVAc. This is possible comparing the DS energy structure (see Table 2) and the polymeric matrixes that were used in the experiment.

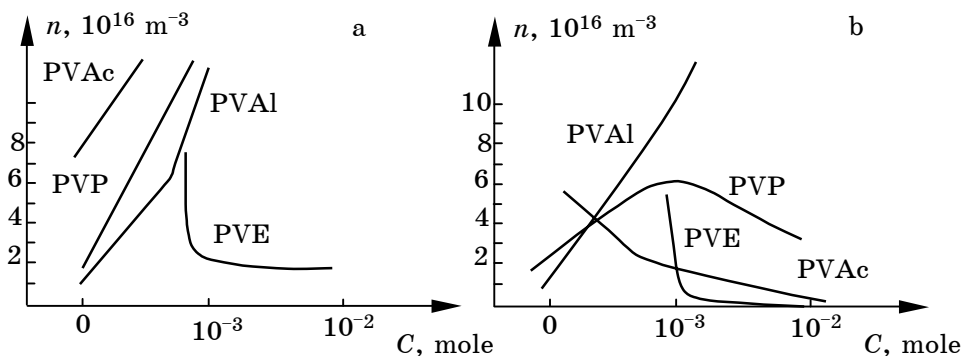
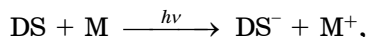


Fig. 2 – Dependence of the current carriers concentration versus the DS concentration in layers: DEAPhD (a); MPhD (b)

From the EPR spectrum at low temperatures (77 K) [13] and from the results of photochemical study at the room temperature [3, 14] it is known that the quantum yield of the electron phototransport on MPhD is bigger than on DEAPhD, i.e., its energy levels are lower than in DEAPhD. So, an electron much more easily passes from matrix on MPhD than on DEAPhD. Quantum-chemical study results of Table 1 confirm this conclusion.

It is possible to determine the presence of an electron phototransport in a system DS/matrix in accordance with reaction



having estimated the thermal effect of the reaction $Q = I_M - E_A^{DS} - h\nu - E_C$. If this value is less zero, the reaction of electron transport passes exothermically. In the other case it is endothermal. Since in polymeric matrix the diazonium salt is not dissociated into ions, the electron affinity energy is decreased more than by 3 eV. Substituting the Table 1 data into expression for Q calculation, we find that the DEAPhD BF_4^- in the lower excited state can capture an electron from PVP ($Q = -0,1$ eV) only. For other matrixes this value exceeds 1 eV. So, the electron transport is possible only under excitation to higher energy levels or from impurities in the polymeric matrix. In the case of the MPhD BF_4^- the electron transport is possible from all matrixes on DS. Here the value of Q is 1,05 eV in PVP and it does not exceed 0,3 eV in other matrixes (the thermal energy and the electric field can overcome such barriers).

So, the largest energy barrier exists between the lowest free energy state of the excited DEAPhD cation and the highest occupied state of PVAI and PVAc matrixes. In this case the photocurrent value has to be the lowest, that is observed experimentally. But the integral absorption of MPhD is less, than of DEAPhD. This is because in PVAc with MPhD the photocurrent value is almost two times less than with DEAPhD.

Photocurrent can be divided into the primary current and the secondary one [9, 10]. The primary photocurrent arises due to the motion of carriers, which are disengaged directly during photoexcitation in the whole illuminated volume. At the same time the secondary photocurrent is often bonded with potential barrier reduction on the surface or in other place because of the primary photocurrent action. As a result of such reduction the possibility of relocation of additional electrons, which were not disengaged directly by light, appears.

The carrier drift mobility is determined from the relation

$$\mu = d^2/U\tau,$$

where d is the film thickness; U is the voltage; τ is the characteristic setting time of a steady-state current.

In general case any investigated sample contains a set of different depth traps, by which current carriers are captured, and as a result they do not participate in motion for some time. The time of staying in these traps can be both less and more than the τ value. In general view the analysis of generated carrier motion in crystals with traps is carried out in [11, 12].

Considering the time dependences for both free and trapped charges the expression for photocurrent changing ΔI was derived:

$$\Delta I = I - I_d = I_s (1 - e^{-t/\tau}),$$

where I_d is the dark current (it arises with energization because of the space charge initiation, impurities level occupation and polarization phenomena); I_s is the saturation photocurrent; t is the sample illumination time; τ is the lifetime of the generated carriers.

From the last expression we can find the τ value:

$$\tau = \frac{t}{\ln(1 - \Delta I/I_s)}.$$

The derived values of the current carrier mobility μ are presented in Table 3 and Table 4.

For DEAPhD one can see the clear mobility increasing with concentration growth in PVAc and PVP, and for MPhD in PVP, PVAc, and PVE.

For DEAPhD in PVE and PVAI the mobility μ initially increases with injection of a small amount of DEAPhD, and then it decreases. For MPhD in PVAc the inverse effect is observed. It could occur due to the influence of intrinsic defects of polymeric matrixes, presence of impurities and non-uniform in thickness DS entry into matrix as well. That is why the injection of a small amount of MPhD at first promotes disappearance of these defects and occupation of impurity levels, which takes all carriers, and mobility decreases.

Table 3 – Current carriers mobility μ ($m^2/(V\cdot sec)$) for DS in polymeric matrixes with different spectrum excitation of the test specimens

μ (DEAPhD), 10^{-12}	ZhS-18		BS-8		UPhS-1		Without filter	
	↑	↓	↑	↓	↑	↓	↑	↓
PVAI (pure)	1,09	1,12	1,48	1,56	1,00	1,16	1,29	1,41
PVAI, 10^{-3}	3,34	3,28	4,34	4,35	4,4	4,08	1,96	3,27
PVAI, 10^{-2}	0,16	0,63	0,19	0,058	0,28	0,091	0,045	0,06
PVAc (pure)	0,097	0,028	0,041	0,031	0,29	0,24	0,34	0,28
PVAc, 10^{-3}	0,09	0,075	0,1	0,8	0,13	0,096	0,12	0,11
PVAc, 10^{-2}	0,2	0,23	0,45	0,39	0,43	0,63	0,18	0,24
PVE (pure)	0,01	0,04	0,06	0,04	0,063	0,13	0,02	0,026
PVE, 10^{-3}	0,35	0,8	0,56	0,62	0,88	0,48	0,3	0,26
PVE, 10^{-2}	0,44	0,14	0,12	0,73	0,19	0,26	0,25	0,19
PVP (pure)	0,07	0,04	0,12	0,18	0,16	0,2	0,09	0,22
PVP, 10^{-3}	0,11	0,11	0,33	0,27	0,19	0,26	0,13	0,22
PVP, 10^{-2}	0,16	0,5	0,34	0,25	0,33	0,28	0,15	0,23

Table 4 – Current carriers mobility μ ($m^2/(V\cdot sec)$) for DS in polymeric matrixes with different spectrum excitation of the test specimens

μ (<i>n</i> - MeO), 10^{-12}	ZhS-18		BS-8		UPhS-1		Without filter	
	↑	↓	↑	↓	↑	↓	↑	↓
PVAI (pure)	1,09	1,12	1,48	1,56	1,00	1,16	1,29	1,41
PVAI, 10^{-3}	0,08	0,17	0,065	0,23	0,1	0,11	0,078	0,085
PVAI, 10^{-2}	0,16	0,21	0,14	0,39	0,12	0,21	0,14	0,14
PVAc (pure)	0,097	0,028	0,041	0,031	0,29	0,24	0,34	0,28
PVAc, 10^{-3}	0,21	0,18	0,13	0,11	0,22	0,14	0,1	0,18
PVAc, 10^{-2}	17,04	19,06	16,3	29,8	10,5	12,8	7,51	8,02
PVE (pure)	0,01	0,04	0,06	0,04	0,063	0,13	0,02	0,026
PVE, 10^{-3}	0,16	0,16	0,16	0,15	0,3	0,22	0,16	0,154
PVE, 10^{-2}	0,17	0,47	0,24	0,19	0,074	0,07	0,084	0,31
PVP (pure)	0,07	0,04	0,12	0,18	0,16	0,2	0,09	0,22
PVP, 10^{-3}	0,23	0,31	0,37	0,6	0,45	0,39	0,23	0,2
PVP, 10^{-2}	0,67	0,47	0,7	0,65	0,7	0,57	0,36	0,36

As for the DEAPhD it could be explained by the following. The electron passage through the substance connected with certain barrier overcoming. The electric field application decreases this barrier value and thereby increases the electron mobility. Under DEAPhD excitation in polymeric matrix the electron detachment from matrix and its excitation by DS cation occurs, that is under illumination a new current carrier – the matrix ion – is formed. In consequence of electron interception the σ_{CN} -connection is decayed and the detachment of N_2 from the DS phenyl ring, where free valence (aryl radical) arises, occurs. This state is extremely unstable and that is why the hydrogen atom from the matrix is captured by the aryl radical. In addition, the DEAPhD ions themselves are present in the sample, which also generate an electric field and thereby reduce the barrier between continuous connection areas. The nature of barriers could be different and,

as a rule, is exactly unknown. One can consider the barrier as a separated phase, a matter, which conducts worse than the basic film. But it is possible, that barriers arise because of the contact potential difference between continuous connection areas of different sized sections [11, 15].

During the further increasing of DEAPhD concentration in PVAI and PVE the ions do not define an electric field any more.

Photocurrent kinetics in different polymeric matrixes, which contain DEAPhD with concentration 10^{-2} mole/dm³, versus the light spectral composition is represented in Fig. 3.

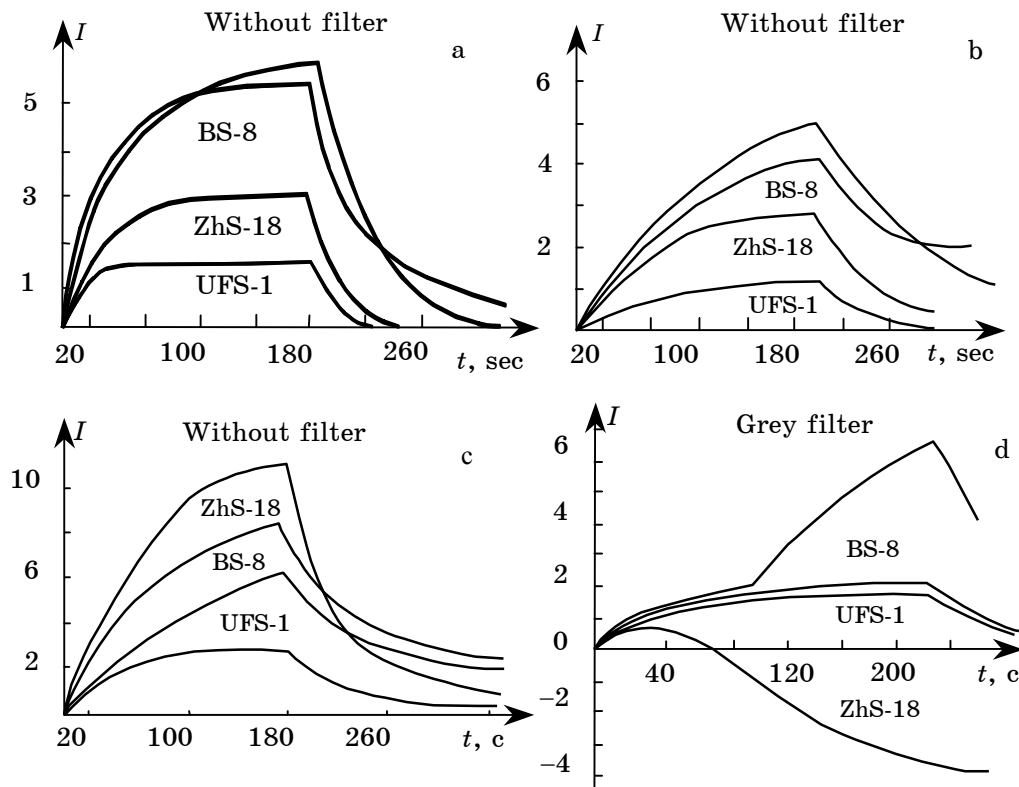


Fig. 3 – Photocurrent kinetics under excitation switching on/switching off for DEAPhD ($C = 10^{-2}$ M) placed into PVE (a), PVAI (b), PVP (c) and PVAc (d) versus the light spectral composition

As seen from Fig. 3, the photoconduction excitation by ultra-violet light from DS absorbing region results in speeding-up the process of photocurrent value saturation in comparison with excitation in visible spectrum (region of layer transparency). It is possible to assume that mechanisms of the current carrier generation in these cases are different. There are considerably less experimental publications about the photo-voltaic effect in organic semi-conductors than about the photoconduction. However this field of study is sufficiently important.

The investigations were done with the same laboratory facility, which was applied for the photoconduction study. Only a thin Teflon film, served

as an insulator, was placed into gap between the sample and the electrode, and thus in the cell the capacitor was constructed. Under lighting by the mercury lamp the current carrier generation and their diffusion are observed. This promotes an electric field appearance in the layer. As a result the potential difference ($U = \int_0^l E(x)dx$) takes place between layer surfaces, i.e., the photoEMF occurs, and its value does not depend on the Teflon film thickness. Induced electric potential under action of a mercury lamp integral illumination of the film without DS had two kinetics: the time-unsteady kinetics of the order of one minute and the steady one (see Fig. 4). Similar components were observed in DS presence, and with DS concentration increasing the photoEMF value also increases. With each next cycle of illumination the photoEMF value decreases. At the same time the optical density decreasing in DS absorption band is observed. In addition the optical density decrease completely correlates with decrease of the photoEMF peak magnitude.

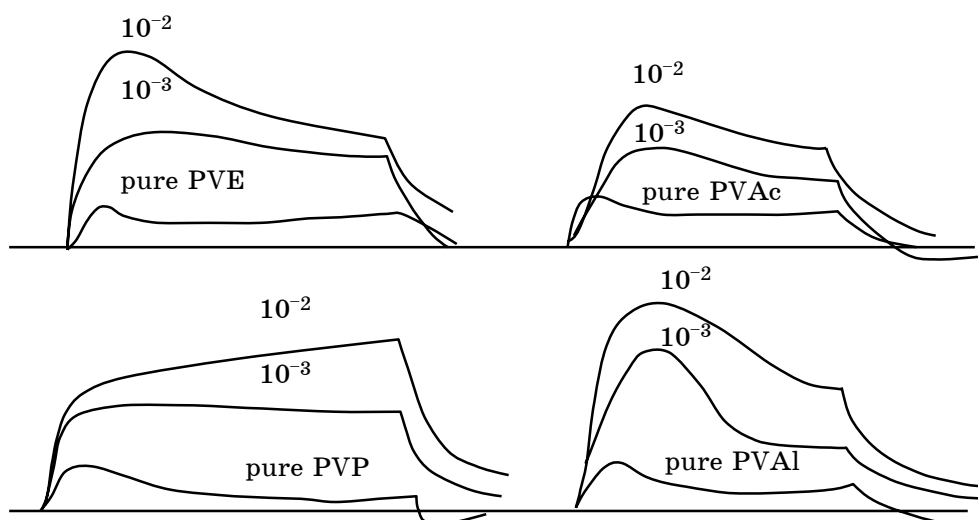


Fig. 4 – The photoEMF kinetics under excitation switching on/off in different polymeric matrixes versus the concentration of MPhD salt

The positive potential on the measuring electrode allows to conclude about the hole conduction of given samples with DS, which is determinative for them. The derived photoEMF values in different polymeric matrixes versus the DS concentration are presented in Table 5. For interpretation of obtained photoEMF results let us to remember, that our samples are non-uniform in thickness. This results in inhomogeneity of traps (impurities) distribution in thickness, which are responsible for the photogeneration and current carrier capturing. Physical properties of the upper and lower surfaces of polymeric layer will be also unequal. If pure polymer was uniform then, most probably, the photoEMF did not appear, since in the absence of absorption the light intensity throughout the sample thickness is equal. Nonuniformity leads to availability of the concentration gradient of photogenerated current carriers and unequal effects on the surfaces. So, the current carrier generation in a volume induces the slow diffusion process of

current carriers and weak photoEMF appearance. The carrier photo-generation on the surface leads to rapid formation of double electric layer of smallish thickness. Since the properties of two surfaces are different with the time of equilibrium attainment and photoEMF value, we will obtain the non-stationary component. Excitation switching off leads to dissolving of two dual electric layers and arising of relaxation process, which we observe during the experiment.

All three described areas of the pure polymeric layer will participate in sample photoconduction.

Table 5 – The value of photoEMF (mV) for different DS concentrations in the polymeric matrixes

Polymer	photoEMF DEAPhD	photoEMF MPhD	Polymer	photoEMF DEAPhD	photoEMF MPhD
PVAL	0,83	0,83	PVE	0,9	0,9
PVAL, 10^{-3}	1,35	1,43	PVE, 10^{-3}	2,02	2,93
PVAL, 10^{-2}	3,08	5,03	PVE, 10^{-2}	4,8	4,43
PVAc	0,9	0,9	PVP	0,98	0,98
PVAc, 10^{-3}	1,25	3,23	PVP, 10^{-3}	1,68	4,35
PVAc, 10^{-2}	3,9	2,85	PVP, 10^{-2}	2,6	11,4

The DS presence in polymeric layer leads to decreasing of excitation intensity with the sample thickness. This fact along with the fact of non-uniform impurity entry into polymeric layer induces appearance both the photoconductivity and the photoEMF. The last one will be purely diffuse.

The complexity of the system polymeric layer-DS depending on the nature of binding polymer can generate different dependences of photogenerated current carrier concentration versus the DS concentration, that we observe in our experiments. These dependences can be caused by the equilibrium concentration value of water vapour in polymer depending on its nature and density, and by dependence of the DS solubility in the polymer solution versus the polymer concentration in the process of its drying as well. So, there are some cases, when DS concentration in the polymeric layer increases both with polymer density increasing and with its fluffing up increasing. And the result will be layer defects removal and decrease of current carrier concentration or inverse process.

Different time of equilibrium process establishing of the polymeric layer photoconduction under illumination both in the transparency region and DS absorbing region is easily explained by the following: generated on the surface the current carriers need more time for movement throughout the sample thickness then generated in the volume ones, where there is the light absorption by DS.

The photocurrent gradual increase instead of the global equilibrium attainment can give the evidence about ion conduction participation (small carrier mobility) into processes under consideration.

So, under MPhD and DEAPhD excitation, placed into polymeric matrixes, one can observe the photocurrent kinetics and the photoEMF, initiated both on the surface and in the sample volume, due to presence of current carriers of two types: the hole and the ion conductions of a matrix in the presence and in the absence of DS.

5. CONCLUSIONS

Thus, the study performed in this work allows us to make the following conclusions:

1. In the polymeric layers, which contain DS solutions of different concentrations, the photoconduction and the photoEMF phenomena are observed. For the first time, using the obtained results we found the mobility and concentration of the current carriers for DS in different polymeric matrixes. The results are satisfactorily could be explained by the electron transport from matrix on DS.
2. The difference in DEAPhD and MPhD energetics has an effect on the photoelectric phenomena at their introduction into different matrixes: the DS introduction into PVAI and PVP increases and into PVE decreases the current carrier concentration n ; as for PVAc matrix its response on MPhD and DEAPhD introduction is diametrically opposite.
3. The energy structure of DS and polymeric matrixes, which explains disagreement in concentrations of generated current carriers for MPhD and DEAPhD in polymeric matrixes, is derived.
4. The mechanism that explains dependence of the current carrier mobility versus the DS concentration is proposed.
5. The current measurements point out the presence of two components in it: the rapid component and the slow one, which are induced by current carriers generation on the surface and in the sample volume. In addition, the slower photocurrent component, as a result of the ion conduction presence, is also observed.
6. The photoEMF measurements showed, that the hole conduction is proper to the polymeric matrix with DS.

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