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# Layers of active carbon with grafted sodium and potassium glycinate derivatives on the surface of PVC film

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**Abstract:** Porous layers from active carbon with macro-molecular cyclic amines with sodium or potassium acetate substituents were synthesized. Layers sewn to the surface of a film of PVC. It is shown that the graft zones around carbon particles consist of luminophore groupings in the form of conjugated rings, including radicals with substituted amino groups, conjugated carbon groups and oxygen atoms binding these groups. The electronic conductivity of the layers and their sorption capacity for the absorption of benzene vapor are measured. It is established that the conductivity of the layer is the higher, the smaller the PVC derivatives, the carbon particles are combined. The conductivity of the layers with potassium ions is greater than that of sodium ions. It is assumed that most of the vapors are concentrated in the pores in the carbon. The sorption capacity of layers with sodium ions is greater than that of potassium ions.

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**1 Introduction:** Porous layers of active carbon with grafted macromolecular cyclic amines with an ethanol substituent (ethanolamine derivatives of PVC), grafted to the surface of a PVC film, electrically conductive and sorption active, are photoluminophore [1]. These properties are due to its structure. Polymer nets are linked through ether groups with carbon atoms on the surface of active carbon particles. Zones of grafting of each particle are formed by their phosphor groupings in the form of jointed cycles of radicals with amino groups, conjugated carbon structures and oxygen atoms of ester groups. The particles, united by grids, are at close distance from each other, allowing an electronic exchange between them. The electronic conductivity and sorption capacity of the layer depends on the ratio «carbon - ethanolamine derivatives».

The structure of the layer is determined by the method of its synthesis. It involves the adsorption of PVC with active carbon in solution at a given ratio «carbon - PVC», grafting PVC to the surface of the carbon, and cross-linking the linear polymer macromolecules to nets of cyclic amines with ethanolamine. In this regard, it is obvious that the characteristics of the layer as a luminophor, its electronic conductivity and sorption activity will depend not only on the ratio of carbon and derivatives of PVC, but also on the nature of the primary amine derivatives, which like ethanolamine can crosslink PVC into nets. Then the substituents of the nitrogen atoms are groups from the corresponding amine. It was shown in [2] that salts of amino acids, in particular glycine, in highly concentrated solutions crosslink PVC into nets from jointed cyclic amines with a substituent as $-CH_2COOM$ group, where $M^+$

is $Na^+$ or $K^+$. Such groups are larger in size than -$CH_2CH_2OH$, and have a different affinity for organic solvents, in particular benzene. It seemed sensible to synthesize active carbon layers with grafted macromolecular cyclic amines with sodium or potassium acetate substituents (sodium and potassium glycinate derivatives of PVC) with the same ratio of carbon and ethanolamine derivatives of PVC sewn to the surface of a PVC film and trace the influence of the substituents nature on the luminescence, electronic conductivity and the sorption capacity of the layers in the absorption of benzene vapor.

The purpose of this work is to synthesize the materials in the form of layers of active carbon with grafted sodium and potassium glycinate derivatives of PVC with various ratios of carbon and PVC derivatives; to investigate the structure of the structural elements of the layer by means of Fourier-transform spectroscopy and luminescent spectroscopy methods; to measure their electronic conductivity and sorption capacity in the absorption of benzene vapor.

## 2. Experimental:

Materials: transparent PVC film (grade PR-M180/09-09/9406, production of China, FUSHIYUAN PLASTIC CO., LIMITED), PVC resin (SG -7, production of China), crushed active carbon (birch active carbon, production of Russia, active surface area 750 $m^2$/g, iodine adsorption activity 60%, porosity by water 1.6 $cm^3$/g),

Reagents: Tetrahydrofuran, benzyl alcohol, triethanolamine, glycine, sodium hydroxide, potassium hydroxide, benzene.

Methods of chemical analysis: Fourier-transform and luminescent spectroscopy, measurement of electrical resistance and sorption capacity.

The luminescence spectra were recorded on a spectrofluorimeter «Fluorolog» (Optics: All reflective optics for high sensitivity at all wavelengths, and for microsamples; Source: 450 W CW Ozone-free Xenon arc lamp (250 to 2500 nm); Monochromators: Czerny-Turner design with plane gratings for optimized focus at all wavelengths and minimum stray light; Excitation grating: 1200 groove/mm blazed at 330 nm; Emission grating: 1200 groove/mm blazed at 500 nm; Bandpass: 0 to 30 nm (single mono, 1200 gr/mm grating), continuously adjustable; 0 to 15 nm (double mono, 1200 gr/mm grating), continuously adjustable; Wavelength Accuracy: ± 0.5 nm; Integration Time: 1 ms to 160 s; Base detector: Photomultiplier R928P, spectral coverage 200 to 870 nm; Reference Detector: UV enhanced silicon photodiode; Water Raman S/N: >30000:1 RMS (> 15,000:1 FSD)).

IR Fourier spectra were recorded on Perkin-Elmer 2000 IR Fourier spectrometer (Detector type MCT, operating range 5 – 40 °C wave length range 7,800 – 600 $cm^{-1}$).

Photomicrographs were obtained using a Motic DMBA 300 optical microscope (Optical System Parfocal distance: 45mm CCIS Optical System (Colour Corrected Infinity System); Observation Tube Siedentopf type Binocular tube 30 (light distribution: binocular 100%, binocular/photo: 0/100); Eyepiece Widefield high eyepoint WF 10X (FN20) with diopter adjustment; Coarse/Fine focusing Control knobs coaxially positioned; movement per rotation: 42mm coarse/0.2mm fine; minimum increment:2μm; minimum scale; coarse motion torque adjustable; upper focus stop incorporated. Substage Illumination 6V/30W Quartz halogen lamp. Filter Blue).

Layer resistance measurements were made using a multimeter MS8233E from HYELEC (DC Voltage: 200mV/2V/20V/200V ±(0.5%+2)/600V ±(0.8%+2); AC Voltage: 2V/20V/200V/600V ±(1.0%+3); DC Current: 200μA/2mA/20mA/200mA ±(1.0%+3)/10A ±(3.0%+3); AC Current:

200µA/2mA/20mA/200mA                 ±(1.2%+3)/10A                 ±(3.0%+5);                 Resistance: 200Ω/2kΩ/20kΩ/200kΩ/2MΩ        ±(0.8%+2)/20MΩ        ±(1.0%+2);        Temperature        (°C):        - 20C~1000C   ±(3.0%+3)). Resistance was measured by 2-probe method. The samples with size 1x1 cm were clamped be two long flat probes and the conductivity and resistance were measured.

Measurement of the adsorption capacity for the absorption of vapors and liquid benzene and hexane was carried out by the weight method.

Synthesis of materials was carried out according to the procedure mentioned in [1]. A sol was prepared from crushed carbon particles with sorbed PVC dispersed in a mixture of benzyl alcohol and triethanolamine. The ratio of the masses PVC:carbon are 1:1, 1:2 and 1:3. Samples of PVC film with a mass m(film) were clamped in a cuvette holder, a dose of sol containing carbon in the amount of m(carbon) was applied to its surface. The film with the sol was held in air until the tetrahydrofuran was evaporated, the PVC sections were grafted to the surface of the carbon by the reaction
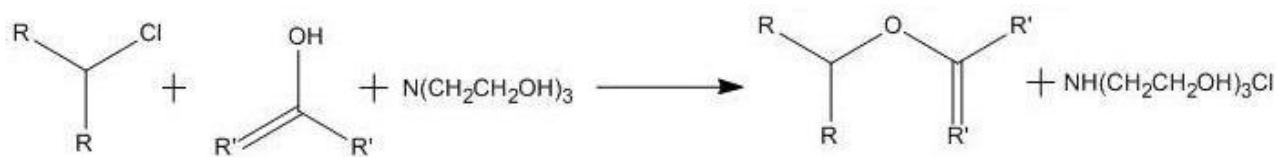


where R – elements of PVC, R´ - elements of active carbon

This reaction was conducted at 105 °C - 110 °C for an hour. Then, 3 mol/l solutions of sodium or potassium glycinate were prepared from glycine and sodium hydroxide and potassium hydroxide. Films with a layer of carbon with grafted PVC were heated in these solutions at 100 - 105 °C for the conversion of PVC into the corresponding derivatives, using the reaction
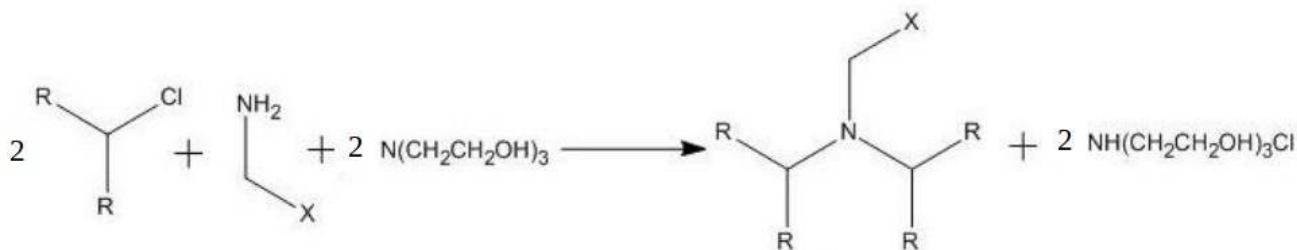


where R – elements of PVC, X – substituent in amine.

Due to this reaction the porous structure of the layer and its suturing to the film surface are formed. Samples of materials were washed in boiling water and dried and their mass was determined. For comparison, in parallel under the same conditions, a material was synthesized in the form of a layer of active carbon grafted with ethanolamine derivatives of PVC attached to the surface of a PVC film. Samples with a layer of carbon and ethanolamine derivatives according to the ratio of PVC: carbon in the sol are designated as ME-1, ME-2 and ME-3, samples with sodium glycinate derivatives of PVC as GN-1, GN-2 and GN-3, and samples with potassium glycinate derivatives of PVC - as GK-1, GK-2 and GK-3.

The composition of the layer was established as follows. According to the synthesis conditions, the mass of the layer is m(layer) = m(sample) - m(film). The layer consists of carbon and PVC derivatives, then the mass fraction of carbon in the layer is equal to the ratio m(carbon)/m(layer). For GN-1, GN-2 and

GN-3, the mass fraction of carbon in the layer (weight %) is 47.7, 64.6 and 73.2%, for GK-1, GK-2 and GK-3 - 43.7, 60.8 and 69.9%, and for ME-1, ME -2 and ME-3 - 51.5, 68.6 and 76.8%. According to the reaction of conversion of PVC into the corresponding derivatives, instead of two chlorine atoms radicals $>N-CH_2CH_2OH$, $>N-CH_2COONa$ or $>N-CH_2COOK$ connect. The average molecular weight of the translated grid link of amines derivatives are 99, 135 and 151, respectively. Using these values and the mass fraction of carbon in the layer of each material, an approximate number of links per gram of carbon (hereinafter γ) was calculated. For ME-1, GN-1 and GK-1, γ ≈ 8.8 mmol, for ME-2, GN-2 and GK-2, γ ≈ 4.3 mmol, and for ME-3, GN-3 and GK-3, ≈ 2.9 mmol .

The structure of the structural elements in the layers was determined using the examples of GN-3 and GK-3. IR spectra are shown in Figure (1), and the luminescence spectra are shown in Figure (2). IR spectra of GN-3 and GK-3 are close. They have a broad band of 1721 $cm^{-1}$ and a band of 1071 $cm^{-1}$, related to C=C and C-O vibrations, C=C-C-C-OR groups forming the grafting zone, as well as bands of about 1594 $cm^{-1}$ and 1478 $cm^{-1}$ antisymmetric and symmetric oscillations in -COO- in anions of amino acids [3, 4]. This corresponds to the fact that the radicals -CH$_2$COO- are a substitute for sodium and potassium of sodium glycinate derivatives of PVC. It should be noted that in the 850-600 $cm^{-1}$ region, there are practically no C-Cl vibration bands in PVC. This means that almost all C-Cl groups were used in grafting and amine formation.
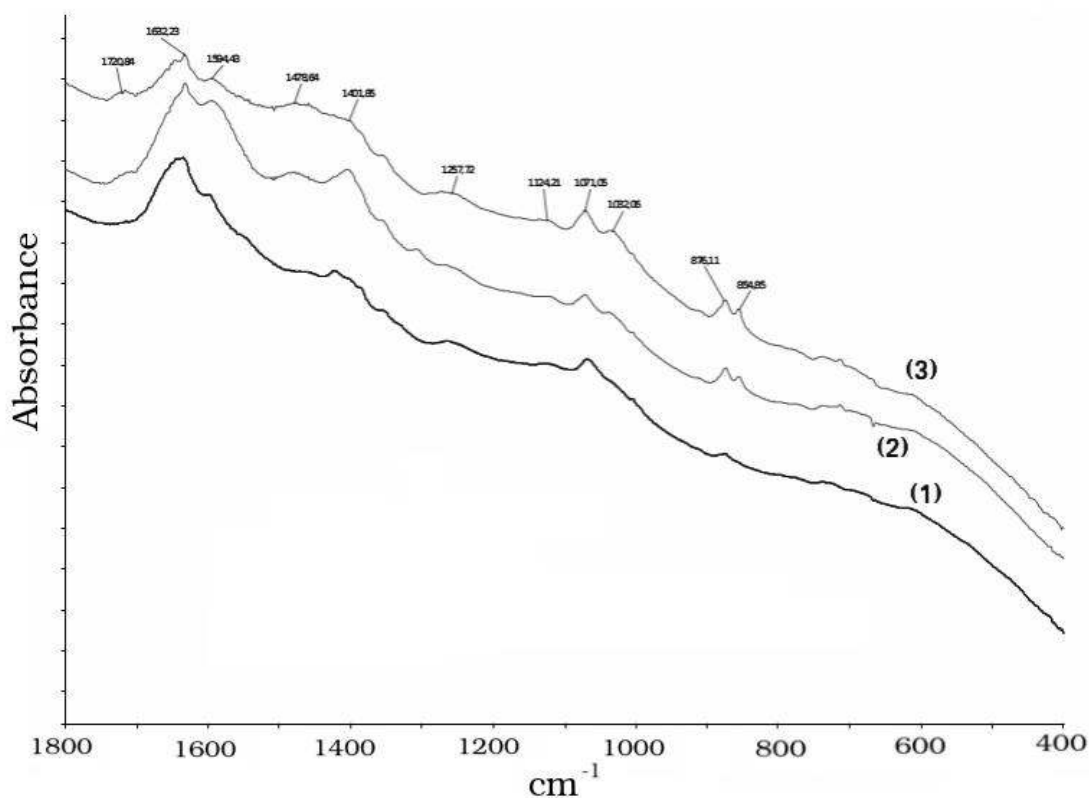


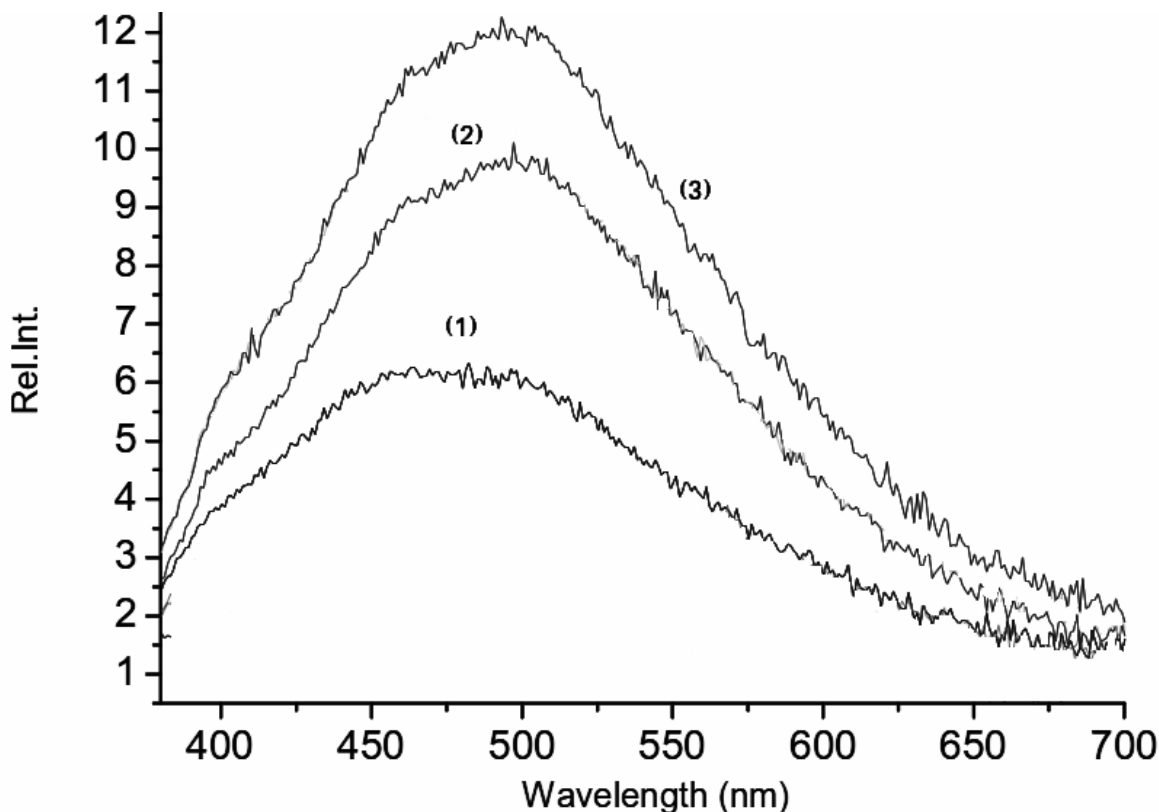Figure (1): IR spectra of the layer in ME-3 (1), GN-3 (2), GK-3 (3).

Figure (2): Luminescence spectra of layers in ME-3 (1), GN-3 (2), GK-3 (3).

The luminescence spectra of GN-3 and GK-3 correlate similarly to the spectrum of EA-3. According to [3], in the grafting zone of ethanolamine derivatives of PVC, luminophore groupings are formed from conjugated carbon structures with radicals with amino groups. Consequently, in the grafting zone of sodium and potassium glycinate derivatives of PVC, similar luminophore groupings are formed. The values of the electronic conductivity and sorption capacity are given in Table (1).

Table (1): Electronic conductivity and sorption capacity of layers.

| Sample | $\sigma$ $10^3$ S | $G_Б$ mmol/g | Sample | $\sigma$ $10^3$ S | $G_Б$ mmol/g | Sample | $\sigma$ $10^3$ S | $G_Б$ mmol/g |
|--------|------------|-----------|--------|------------|-----------|--------|------------|-----------|
| GN-1 | 0.75 | 10.41 | GK-1 | 0.85 | 9.80 | ME-1 | 0.35 | 13.4 |
| GN-2 | 3.45 | 12.89 | GK-2 | 4.76 | 10.45 | ME-2 | 1.69 | 10.62 |
| GN-3 | 5.55 | 12.77 | GK-3 | 5.88 | 11.34 | ME-3 | 2.08 | 9.83 |

## 3. Results and Discussion

Investigation has shown that the replacement of -CH$_2$CH$_2$OH groups by CH$_2$COONa and -CH$_2$COOK groups led to a change in the characteristics of the layers.

As can be seen from Figure (2), the bands in the luminescence spectra of GN-3, GK-3, compared with the luminescence spectrum of ME-3, shifted to the long-wavelength region from 473 nm to 595 ± 598 nm. This indicates that the effect of the -CH$_2$COONa and -CH$_2$COOK groups in cycles in the grafting zone is somewhat different than the -CH$_2$CH$_2$OH group. The intensity of the bands in the spectra of GN-3 and GK-3 increased approximately 1.5 and 1.9 times more than in ME-3. Since $\gamma$ is the same in these layers, it can be assumed that the graft zone forms the same number of phosphor groups. Given the

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differences in the size of these groups, it can be assumed that as the size increases, the conformational oscillations in the cycles are limited, which reduces the energy dissipation for exciting conjugated structures in the carbon.

As can be seen from Table (1), for each derivative, the value of σ increases with decreasing γ. This is due to the fact that when carbon particles are combined with a smaller number of nets, the packing of carbon particles becomes dense. At the same value. At each value of γ, the conductivity of the layers increases in the series -CH$_2$CH$_2$OH -CH$_2$COONa -CH$_2$COOK, where the value of σ for the layers with ethanolamine derivatives is 2 or more times lower than in the case of sodium glycinate derivatives. This can be explained by the fact that as the size of the substituent increases, the packing density of carbon particles increases.

When discussing the data of Table (1) on the sorption capacity of the layers, attention was paid to the features of their porous structure. On the surface and between the particles of carbon there are pores with walls made of PVC nets. Through the cavities of cycles with amino groups, these pores turn into pores in zones of grafting with walls of cycles, including radicals with amino groups, conjugated carbon structures and ether groups. These pores are docked with pores in the corner. The volume of pores in the carbon in all materials with the same value of γ is approximately the same. The number of pores of the first and second types is the greater, the greater γ. For the same γ, the larger the size of the substituent, the smaller the volume of these pores. Sorption of vapors in the pores of the first and second types is based on the formation of host-guest molecular complexes between cyclic amines and/or cycles with carbon structures in the grafting zones and sorbed molecules. The complexing capacity of the cycles, that is, their affinity for the molecules to be sorbed, will depend on the nature of the substituents. From Table. 1 that the values of G(vapour) are practically not correlated with the values of γ. This suggests that most of the vapors are concentrated in the pores in the carbon. This is possible if the energy of sorption of benzene in carbon is greater than the energy of the formation of molecular complexes. Then the benzene molecules will be retained by other pores after filling the pores in the carbon. The values of G(vapour) for GN-1 and GK-1 are less than for GN-2 and GK-2 and for GN-3 and GK-3, while G(vapour) in ME-1 is more than in ME-2 and ME-3. It is possible that -CH$_2$COONa and -CH$_2$COOK groups create steric obstacles for the transition of benzene molecules to the pores of carbon. At the same time, the -CH$_2$CH$_2$OH group, due to a different binding of benzene molecules, promotes its transition to pores of carbon. The values of G(vapour) in GN-1, GN-2 and GN-3 are somewhat larger, in GK-1, GK-2 and GK-3, respectively. This can be explained by the fact that the pores with radicals -CH$_2$COONa have a larger volume than ones with -CH$_2$-COOK.

**4. Conclusions:** The present experiments showed that the characteristics of active carbon layer with grafted net derivatives as a luminescent substance, its electronic conductivity and sorption activity depends on the nature of the substituents at nitrogen atoms in PVC derivatives.

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