

POLYANILINE-BASED SENSORS FOR SOLUTION COMPONENTS

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ABSTRACT

Polyaniline (PAN) in the poorly conductive base form was used in sensors for solution components as a sensitive layer on insulator and transistor substrates. The coatings were obtained by casting PAN base solution in N,N-dimethylacetamide. High sensitivities were obtained to ethanol in hexane and a stable radical 4-acetylamin-2,2,6,6-piperidine-1-oxyl (ATPO) in ethanol, using an 'active' transistor structure as well as to ATPO or citric acid in ethanol using PAN resistor structure. According to 3 cm and 2 mm range ESR data there are radicals in PAN base film. Appearance of the second signal in 2 mm range ESR spectra below 150 K suggests the existence of two phases in PAN base film.

INTRODUCTION

Utilization of conducting polymers in chemical sensors for organic vapors [1-3] and inorganic gases [4] has recently been investigated. The resistance of polyconjugated polymers in doped and undoped states is known to range within many orders of magnitude and consequently the polymer can act in a sensor as a variable resistor. Transistor structures can also be used as chemical sensors [5] since the potential barrier of the base of a transistor, and hence the resistance, can alter upon interaction with a medium. We assume that in this case a layer of conducting polymer on the transistor structure could act as mediator changing the values of response. One of the most promising conducting polymers, polyaniline (PAN) could be a good mediator and a sensor component in the base state (PAN-B) because of the existence of electron donor (amino-) and acceptor (quinone diimino-) sites. In its salt form PAN has been shown to be sensitive to vapors of ethanol or acetone [3]. But in solution uncontrollable dedoping of the polymer and reactions with the acid can take place.

In this paper, the sensoric properties of polyaniline base films on non-conductive and transistor substrates in terms of detection of three organic substances of different types, namely, ethanol, citric acid, a stable radical ATPO and some others are studied [6].

EXPERIMENTAL

A PAN salt was synthesized by oxidation of 0.5 M aniline solution in aqueous 1M HCl with peroxodisulfate (1 mole per mole of aniline). Two techniques of coating (A and B) were studied [6]. A PAN-A layer was formed after drying at 60-80 C when the reaction proceeded just on the replace of the substrate. PAN-B films were obtained by casting solutions of a dried PAN base (aqueous ammonia treated PAN salt) in N,N-dimethylacetamide. According to the IR spectra (IR-75, GDR) PAN-A is a salt of PAN and PAN-B film is similar to the base of PAN. The salt and the base can be easily transformed into each other, so PAN-A and PAN-B were compared in the same state. SEM (Tesla BS-300, Czechoslovakia) and conductivity measurements (four-probe) show a more irregular structure and poorer interparticle contacts in the PAN-A coating than in the PAN-B film. That is why only the PAN-B film was studied as a sensor component.

The substrates used were silicon transistor structures KT827 with 'active' and 'passive' connection and a glass-cloth base laminate (GCLB) with two copper electrodes spaced by a 1 mm-wide gap. All the sensors were connected by a differentiating circuit with a multistage amplifier. ESR spectra were obtained using a 3 cm range (EPR-8) and a 2 mm range [7] spectrometers (both of the Institute of Chemical Physics, USSR, design).

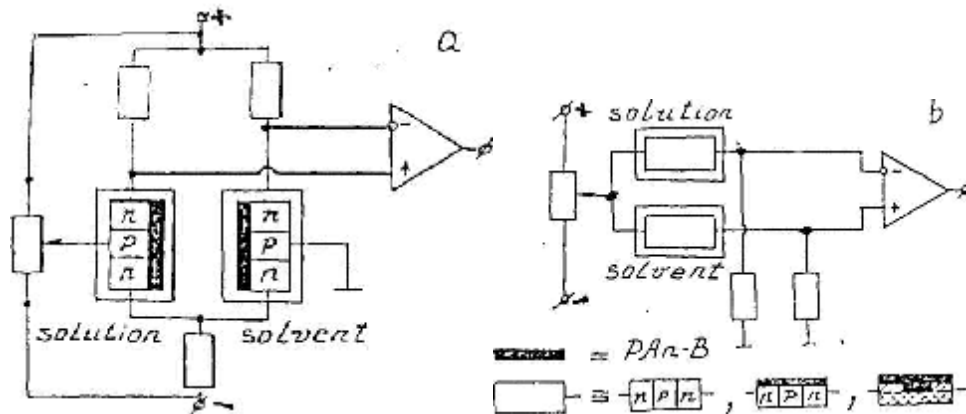


Fig. 1. Differentiating circuit with a multistage amplifier, a) 'active' scheme for transistors, b) 'passive' scheme for transistors and PAN on GCLB.

RESULTS

Ethanol in hexane (Fig. 2a)

The 'passive' transistor (with or without PAN) and the PAN resistor structures are practically insensitive to ethanol concentration changes in hexane; their characteristics are almost horizontal and non-monotonous. This implies that no appreciable charge transfer between the ethanol and the above structures occurs.

The 'active' transistor structure has a noticeable sensitivity but the response is non-linear, with a steepness of 590 V.l/mol in the initial region and a tendency to saturation at concentrations higher than 0.4 mM. PAN-B casting changes the sign of the response, i.e. the polymer does not act synergetically with the transistor structure. The steepness decreases to 230 V.l/mol but the characteristic has a lower curvature. The latter sensor has a B20 V.l/mol -steep response to acetone and is also sensitive to KI in an aqueous solution.

Probably the PAN-B film can form the charge transfer complexes with both the base of a transistor and polar substances such as ethanol in solution to give changes of the response.

Citric acid in ethanol (Fig. 2b)

The sensitivity to citric acid is, with all the structures, higher than that to ethanol and the characteristics have lower curvatures. PAN slightly increases the sensitivity of the 'passive' transistor sensor thus acting synergetically with the transistor structure, but both response values are relatively low, no more than 200 V.l/mol.

It is noteworthy that rather a steep (535 V.l/mol) and perfectly linear (for the studied range of concentrations) response is attained for a simple resistive PAN sensor. This should be due to the protonic acid doping of the PAN base to more conductive salt states with a significant drop in resistance.

ATPO in ethanol (Fig. 2c)

As in the case of ethanol in hexane, 'passive' transistors with or without PAN are practically insensitive. The characteristic of the 'active' transistor (without PAN), being rather steep initially (1200 V.l/mol), becomes horizontal at concentrations higher than 0.06 mM. PAN acts synergetically increasing the steepness of the response up to 1B30 V.l/mol in the initial concentration range and keeps the characteristic increasing to at least 0.15 M. The response of the resistive PAN sensor is less steep (800 V.l/mol) but has a lower curvature over the whole range of concentrations studied.

A comparison of the results for ATPO and ethanol shows that interaction of the radical with the sensors is of another type. In the case of PAN-B, interaction of the ATPO radicals in solution with the radicals of the polymer could take place if the latter ones exist. This led us to conduct an ESR study of the PAN-B film

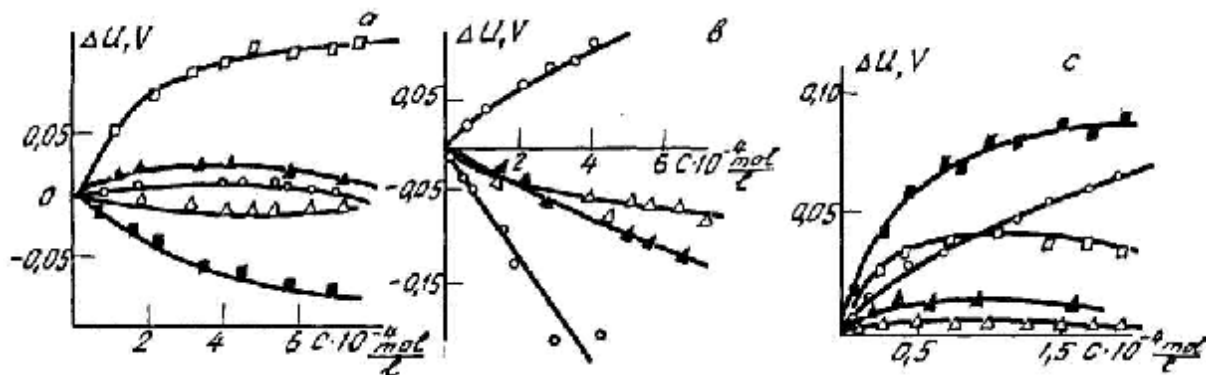


Fig. 2. Response of the sensors to a) ethanol in hexane, b) citric acid and c) ATP0 in ethanol vs. concentration. - 'passive' transistor, - PAN-B on the 'passive' transistor, - PAN-B on the 'active' transistor, - 'active' transistor, - PAN on GCLB.

ESR-spectra of PAN-B (Fig.3)

3 cm and 2 mm range ESR spectral studies of a PAN-B film were carried out. The shape of the signal is temperature independent down to 77 K. Doping with 0.1 M sulphuric acid leads to narrowing of the signal to 2.5 G. In the 2 mm range, lowering the temperature leads to an asymmetry of the signal (below 345 K) with the

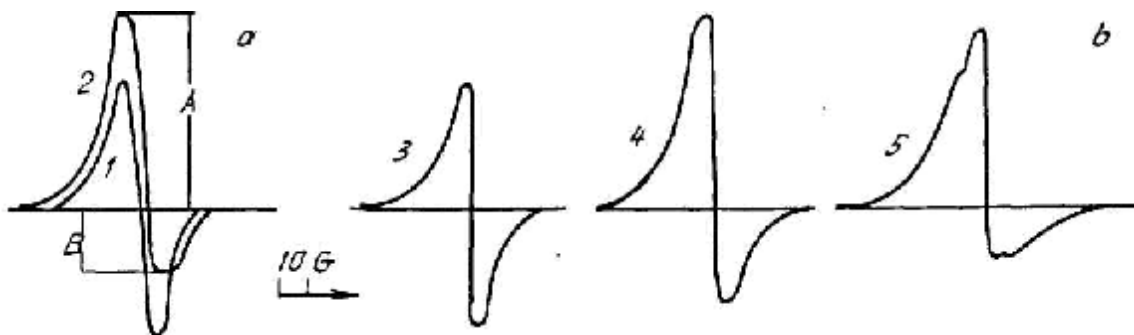


Fig. 3. 2 mm range ESR. spectra of a) PAN-A at 350 K (1) and 220 K (2) and b) PAN-B at 300 K (3), 270 K (4) and 130 K (5).

line shape factor (A/B) increasing up to 4 (130 K). Below 150 K the ESP. signal is a superposition of two lines with $g = 2.00310$ and $H_{pp} 5$ and 12 G, respectively. This may be due to the existence of two solid phases in PAN-B film [8]. The temperature dependence of the PAN salt ESR spectra differs from that of PAN-B.

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