Dehydrochlorination of interpolymer complexes and composites of polyanilines with poly acids

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The temperature ranges of dehydrochlorination (50–180°C) and degradation (320°C and above) of polyanilines have been determined. A study has been made of the thermal stability of polyaniline interpolymer complexes and composites in a wide temperature range. The activation energy of the dehydrochlorination of doped polyaniline specimens has been established.

Conductive polymers are attracting a great deal of attention among researchers owing to their unusual electronic properties and the prospects of their practical use. Polyanilines possess stability in the environment and are synthesised comparatively easily both chemically and by electrochemical methods. As a result of the interaction of polyanilines with low-molecular-weight acids in the protonated state, they possess a conductivity of up to $10^{-2}$ Ω$^{-1}$ cm$^{-1}$. Furthermore, polyaniline and poly-otoluidene are very much characterised by a fundamentally new type of doping – protonation by polymeric acids, during which there is no change in the number of electrons in the main chain of the polymer, as occurs in the case of other conductive polymers.

A study has been made of the kinetic laws governing processes of protonation and the thermal stability of interpolymer specimens of polyanilines. The heat resistance of polyaniline has been described in the literature [3], but the authors investigated the behaviours of polyaniline only at a single temperature (150°C). In the present investigations, we examined the behaviour of polyanilines in a wide temperature range.

The results of the conducted investigations of the kinetic dependence of current passing through pellets of polyanilines on the doping time showed that, with increase in the mole fraction of vapours of hydrochloric acid HCl, the doping rate increases (Figure 1). At high concentrations of HCl in the liquid phase, liquid–vapour equilibrium is established fairly rapidly, and therefore the mole fraction of HCl vapours in the process of interaction with the surface of polyanilines can be considered to be constant. In this case, the effective rate constants of the reaction of protonation of polyaniline specimens has been established.

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SUMMARY

The temperature ranges of dehydrochlorination (50–180°C) and degradation (320°C and above) of polyanilines have been determined. A study has been made of the thermal stability of polyaniline interpolymer complexes and composites in a wide temperature range. The activation energy of the dehydrochlorination of doped polyaniline specimens has been established.
PANI: HCl pellet is fairly intense, which is due to the high volatility of ammonia from the aqueous solution. It must be pointed out that the same polymer specimen can undergo repeated treatment with HCl and ammonia NH₃ vapours, but, after a certain number of cycles, the influence of NH₄Cl formed on the pellet surface is observed.

For a more thorough understanding of the processes occurring during the doping of polyanilines, we studied the kinetics of the PANI:HCl reaction by electron paramagnetic resonance spectroscopy (EPR). EPR investigations were conducted in a closed ampoule, on the bottom of which an aqueous solution of hydrochloric acid was poured. A polyaniline polymer pellet was suspended by a thread (at a distance of 20 mm) above the level of the evaporating HCl. The mole fraction of equilibrium vapours of HCl can be determined from reference data.

As a result of the interaction of polyaniline powder with hydrochloric acid, there was an increase in intensity, a narrowing of the peak, and a certain shift in the g-factor of the EPR signal. All changes are due to an increase in the concentration of localised paramagnetic centres on the polymer chain owing to the formation of cation radicals. The intensity \( J \) of the EPR signal as a function of the doping time corresponded to different sample weights of the polyaniline powder (Figure 2). Three characteristic regions of change in signal intensity were observed: in the first region, a roughly linear dependence of signal intensity \( J \) on time was observed, and here its slope depended little on the weight of the sample; in the second region, it increased sharply; in the third region, the dependence became linear. The transition points from the first to the second region depend on the weight of the sample. However, if normalisation per unit mass of the polyaniline is carried out, then transition is observed on the achievement of roughly identical values of the concentration of spins, which is equivalent to an identical degree of dosing. The non-linear nature of the dependences seems to be due to differences in the mechanisms of the kinetics of doping for different regions.

The first region reflects the kinetics of doping of polyaniline with rate constant \( K_1 \). On achievement of a certain critical concentration of spins, a reaction with \( K_2 \) begins to proceed. Saturation of the run of the dependence in the third region seems to be due to two factors: saturation of the degree of doping and transition of some of the Curie spins to Pauli spins owing to the formation of a conductivity zone.

The data obtained indicate that increase in the EPR signal of the upper polyaniline layer is observed only after saturation of the lower specimen with acid is achieved. This indicates that the lower specimen absorbs all the evaporating acid before this instant. This is also borne out by the fact that the slope of the dependences in the first region is not dependent on the weight of the sample. The difference in the run of the dependences of the of EPR spectra on time in the first and second regions indicates the difference in the natures of interaction of polyaniline with HCl. As the evaporation is constant, the polyaniline powder absorbs all incoming HCl until saturation of the specimen (Figure 1, third region). It must be pointed out that paramagnetic centres are formed on the polyaniline chain, and that not all HCl molecules interact with polyaniline. Only some of them, it seems, are sorbed by the polymer, without the formation of a chemical bond with nitrogen of the polyaniline chain – a first-order reaction. The dependence of the logarithm of the rate constant of the reaction on inverse temperature has a linear form, i.e. the Arrhenius equation is obeyed. The activation energy of dehydrochlorination that was calculated from the slope of this dependence was 26 kJ/mol. The given quantity was determined for the first time and, it seems, requires confirmation using different methods of investigation.

REFERENCES