Acid-base properties of poly(1-vinylazoles) in aqueous solution

N. L. Mazyar,[a] V. V. Annenkov,[b]★ V. A. Kruglova,[b] S. M. Anan'ev,[b]
E. N. Danilovtseva,[a] A. V. Rokhin,[b] and S. V. Zinchenko[a]

[a] *Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences,*
1 ul. Favorskogo, 664033 Irkutsk, Russian Federation.
Fax: +7 (395 2) 39 6046. E-mail: admin@irioch.irk.ru
[b] *Department of Chemistry, Irkutsk State University,*
126 ul. Lermontova, 664033 Irkutsk, Russian Federation

The interaction of poly(1-vinylimidazole) and poly(1-vinyl-1,2,4-triazole) with HCl and alkalies in aqueous and water-salt solutions was investigated by potentiometric titration, viscosimetry, ^{1}H and ^{13}C NMR, and UV spectroscopy. The effect of the nature and concentration of low-molecular counterions was found. The interaction of poly(1-vinylazoles) with the acid results in the protonation of the azole cycle. The interaction of poly(1-vinylazoles) with alkalies is stipulated by the capability of the pyridine N atom of forming a coordination bond with the metal ion and that of the unsaturated π-system of the heterocycle of coordinating with the anions.

Key words: poly(1-vinylazoles), poly(1-vinylimidazole), poly(1-vinyl-1,2,4-triazole), acid-base properties.

Poly(1-vinylimidazole) (PVI) and poly(1-vinyl-1,2,4-triazole) (PVT), *viz.*, water-soluble polymers with several fruitful properties, are used for the preparation of polymeric dyes, catalysts, and ion-exchange resins.[1] They are also used as models of biologically active macromolecules,[2] drug carriers,[3] and quenching media.[4] The technical characteristics and biological activity of these polymers are mainly determined by their acid-base properties.

Poly(1-vinylazoles) (PVAz) contain two active centers: a lone electron pair of the pyridine N atoms, which exhibits donating properties,[5,6] and an unsaturated π-system of the heterocycle, which is characterized by withdrawing properties. Intra- and intermolecular interactions between the azole cycles, capable of acting as both electron donors and π-acceptors, have been found.[7,8]

In this work, we studied the interaction of PVAz with low-molecular strong electrolytes (HCl and alkali) in dilute aqueous and water-salt solutions in order to reveal the character of the interaction of the azole groups of the polymers with the H^+, OH^-, and alkali metal ions. The influence of the azole cycle structure on its electron-donating and electron-withdrawing properties is discussed.

Experimental

Polymers PVI and PVT were synthesized from the corresponding monomers in the presence of azoisobutyronitrile (1% of the monomer weight) in tubes in an inert gas atmosphere at 60 °C for 48 h without a solvent. The obtained polymers were dissolved in DMF, re-precipitated by diethyl ether, and dried *in vacuo* to constant weight. The yield was 85—90%. The degree of polymerization determined viscosimetrically by the Mark—Kuhn—Houwink—Sakurada equation with the K and α values published previously[9,10] was 750 for PVI and 850 for PVT.

Low-molecular salts, acids, and bases (reagent grade) were used. A solution of HCl (0.1±0.001 mol L^{-1}) was prepared from the standard solution TU 6-09-2540-79. The exact concentration of alkalies was determined by titration with the solution of HCl.

Potentiometric titration was carried out on a Hanna HI8520 pH-meter in a thermostatted cell in a nitrogen atmosphere at 20±0.1 °C. Bidistilled water was used to prepare solutions of polymers. The absolute error of pH measurements was 0.01. Viscosimetric studies were performed on a Ubellohde capillary viscosimeter at 20±0.1 °C, varying the ratio acid (base)—PVAz at a constant polymer concentration. The divergence of the results of potentiometric and viscosimetric measurements in parallel experiments was ≤1%.

^{13}C NMR spectra were recorded on a VXR-500S spectrometer (Varian, 126 MHz) with noise proton decoupling, detecting 10000 cycles with a relaxation delay of 5 s and a pulse of 90° in a D_2O solution. ^{1}H NMR spectra were obtained on a DPX-400 spectrometer (Bruker, 400.13 MHz) in a solution of D_2O. The polymer concentration was 1%. The position of signals in the NMR spectra were determined relative to the external standards, *viz.*, sodium 4,4-dimethylsilapentanesulfonate (^{1}H) and $MeNO_2$ (^{13}C). UV spectra were recorded on a Specord UV—Vis spectrometer in 0.5-mm quartz cells.

The degree of ionization of the conjugated acid PVAz (α) was calculated by a formula analogous to that presented previously[11]:

$$\alpha = 1 - \frac{\left\{C_{\mathrm{HCl}}V_{\mathrm{HCl}}/(V_0 + V_{\mathrm{HCl}}) - [\mathrm{H}^+] + [\mathrm{OH}^-]\right\}\cdot(V_0 + V_{\mathrm{HCl}})}{C_{\mathrm{PVAz}}V_0},$$

where V_0 is the initial volume of the titrated solution, C_{PVAz} is the initial concentration of the polymer, and C_{HCl} and V_{HCl} are the concentration and added volume of the acid, respectively.

To calculate pK, we used the formula

$$\mathrm{p}K = \mathrm{pH} - \log[\alpha/(1 - \alpha)].$$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2047—2052, December, 2000.

Results and Discussion

Potentiometric titration of PVAz with a solution of HCl showed that the curves pH *vs.* V_{HCl} for solutions of PVI and PVT lie much higher than those for the pure acid at the corresponding concentration of PVI and PVT in water (Fig. 1). This indicates the addition of a proton to the pyridine N atom of the azole cycle (Scheme 1).

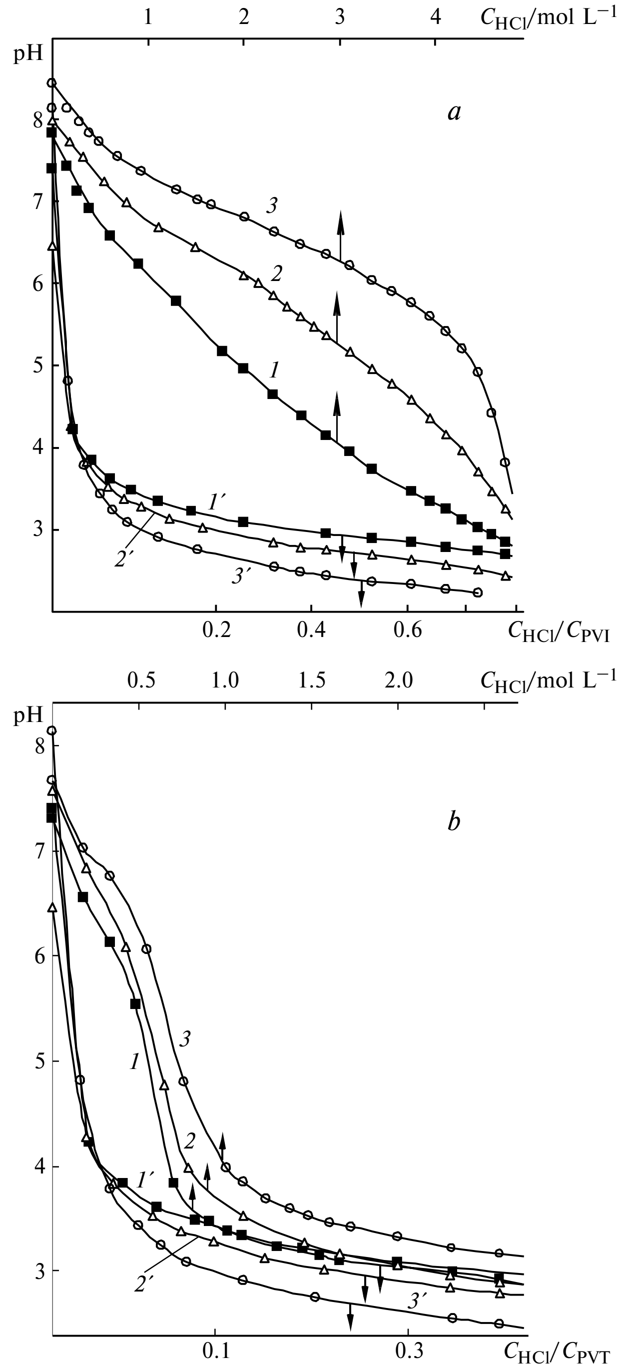
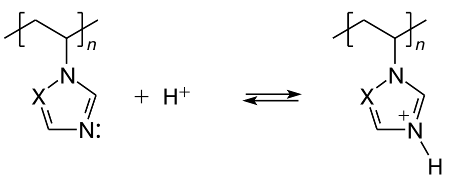


Fig. 1. The plots of the pH *vs.* HCl concentration for solutions of PVI (*a*) and PVT (*b*) without salt additives (*1*, *1′*) and in the presence of 0.1 (*2*, *2′*) and 1.0 mol L^{-1} (*3*, *3′*) NaCl: *1*—*3*, a solution of PVAz; *1′*—*3′*, a solution of HCl with the corresponding concentration.

Scheme 1



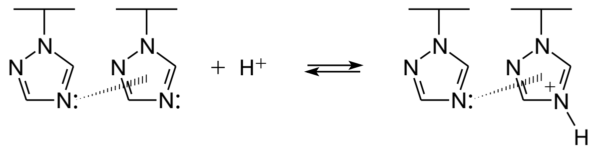
X = CH (PVI), N (PVT)

Despite the presence of two N atoms capable of interacting with a proton in the triazole cycle, it is probable that only the N atom in position 4 participates in the reaction, being the most electronegative.[7,8] For a PVI solution, higher pH are observed up to the equimolar ratio of the concentrations of HCl and polymer. A PVT solution has a higher pH at the ratio of the concentrations of the acid to polymer ≤0.1. The introduction of a low-molecular salt into the solution (see Fig. 1, curves *b*, *c*) increases the basicity of PVAz due to a decrease in the electrostatic effects, which is characteristic of weak polyelectrolytes.[12]

The titration curves of solutions of PVI and PVT in the coordinates of the p*K* of conjugated acid *vs* α (Fig. 2) differ substantially. With increasing the deprotonation degree of the conjugated acid PVI, its p*K* increases monotonically. After a solution of PVT was neutralized with the acid by 5—6%, its basicity decreased by 2—3 orders of magnitude. This phenomenon could be explained by the conformational transition accompanied by the condensation of the structure of the PVT molecules, an increase in the positive charge density, and, correspondingly, a decrease in the basicity. However, the data of viscosimetric measurements (Fig. 3) indicate a similar character of viscosity changes in solutions of PVT and PVI at the initial stages of protonation. The specific viscosity uniformly increases, which is due to an increase in the size of the macromolecular tangles with protonation.

Meanwhile, the pK_0 values of the abstraction of the last proton from the conjugated acids (Table 1) obtained by the extrapolation of the plot of p*K* *vs.* α to $\alpha = 1$ are sufficiently close for PVI and PVT. A relatively high basicity of unprotonated PVT is rather unexpected if we take into account the considerable difference in basicity of the PVAz monomers (pK_a of the conjugated acid 1-ethylimidazole is 8.9, and that of 1-ethyl-1,2,4-triazole is 4.3 [13]). This fact can be explained using the known data[7,8] on the donor-acceptor interactions between the azole units in PVAz in the condensed state, which are more characteristic of PVT rather than PVI. When PVT is dissolved in water, some of these bonds are retained, and the azole units that act as acceptors of the electron density acquire an elevated basicity (Scheme 2).

Scheme 2



An increase in the positive charge at the PVT chain inevitably results in the decomposition of bonds between the triazole units when the macromolecular tangle is swollen during protonation, and the basicity of PVT decreases dramatically. The reasons for a relatively low basicity of PVI (pK_0 = 5.6) as compared to that of the low-molecular analog (pK_a = 8.9) remain unclear.

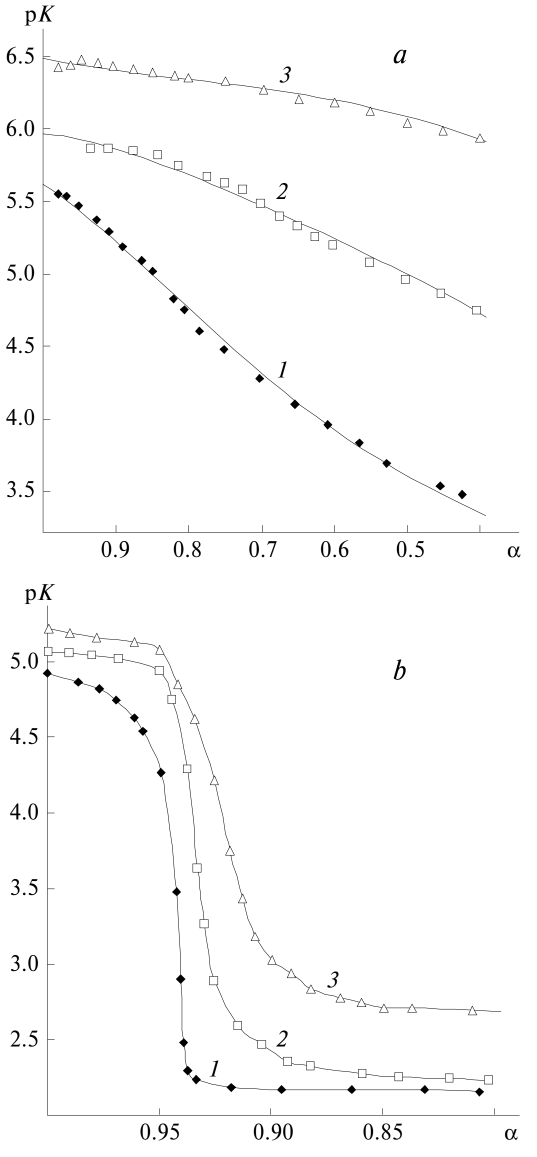


Fig. 2. The plots of the pK *vs.* ionization degree (α) of PVI (*a*) and PVT (*b*) without salt additives (*1*) and in the presence of 0.1 (*2*) and 1.0 mol L^{-1} NaCl (*3*).

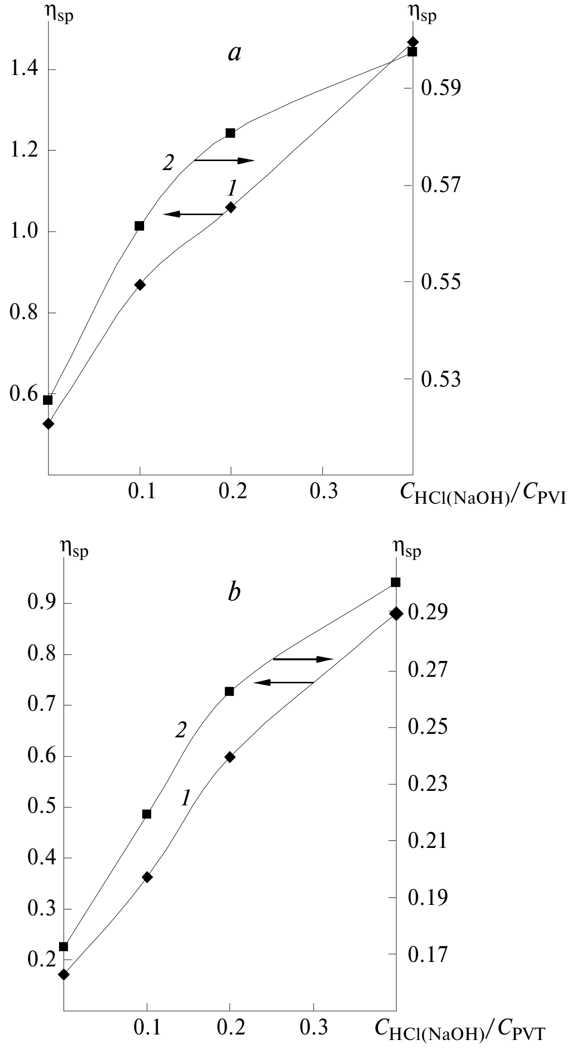


Fig. 3. Specific viscosity (η_{sp}) as a function of the ratio of concentrations of HCl, NaOH, and PVAz for solutions of PVI (*a*) and PVT (*b*): *1*, HCl; *2*, NaOH; C_{PVAz} = 0.1 mol(base) L^{-1}.

When an alkali is added to solutions of PVAz, the pH also differs from that of an alkaline solution with the corresponding concentration (Fig. 4). At a low concentration of a low-molecular base, the pH values of PVAz solutions are lower than those for a pure alkaline solution. Then the titration curves of PVAz solutions shift to a more basic pH region. The effect of pH decreasing is more pronounced for PVT.

Table 1. pK_0 of the abstraction of the last proton from conjugated polyacids PVAz

C_{NaCl} /mol L^{-1}	pK_0	
	PVT	PVI
0	4.9	5.6
0.1	5.1	6.0
1.0	5.2	6.5

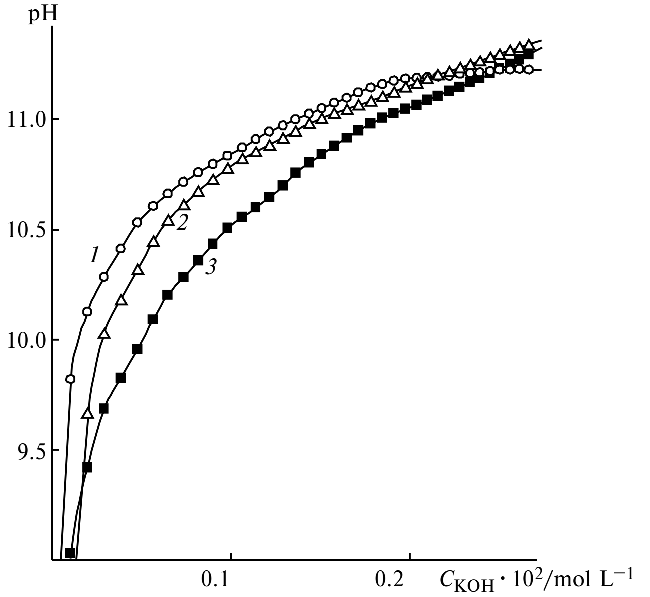
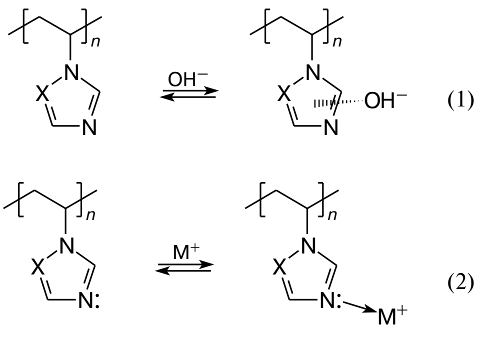


Fig. 4. The plots of the pH *vs.* KOH concentration: *1*, a solution of KOH with the corresponding concentration; *2*, titration of a solution of PVI; and *3*, titration of a PVT solution.

The azole cycles can interact with alkalies in aqueous solution *via* two routes (Scheme 3).

Scheme 3



The interaction of the π-system with the hydroxide anion (reaction (1)) should decrease pH. However, the coordination of the alkali metal cation with the lone electron pair of the pyridine nitrogen atom (reaction (2)) enhances the activity of the OH^- anions and, correspondingly, pH.

The titration of PVAz with solutions of various alkalies (Fig. 5, curves *1—3*) showed that on going from KOH to LiOH the titration curves shifted to an alkaline region relative to pure alkalies. This fact seems quite reasonable if we take into account the increase in the coordination capability of cations in the series $K^+ < Na^+ < Li^+$ and, hence, the more considerable contribution of reaction (2). As should be expected, the influence of the cation nature is more pronounced for PVI containing the more electron-donating N atoms.

With the ionic strength increasing, the titration curves of PVAz shift to the alkaline region as compared to those obtained without low-molecular salt additives (see Fig. 5, curves *2*, *2′*, *2″*). When salts are added, the Na ion of the salt competes with the OH^- anion to suppress reaction (1).

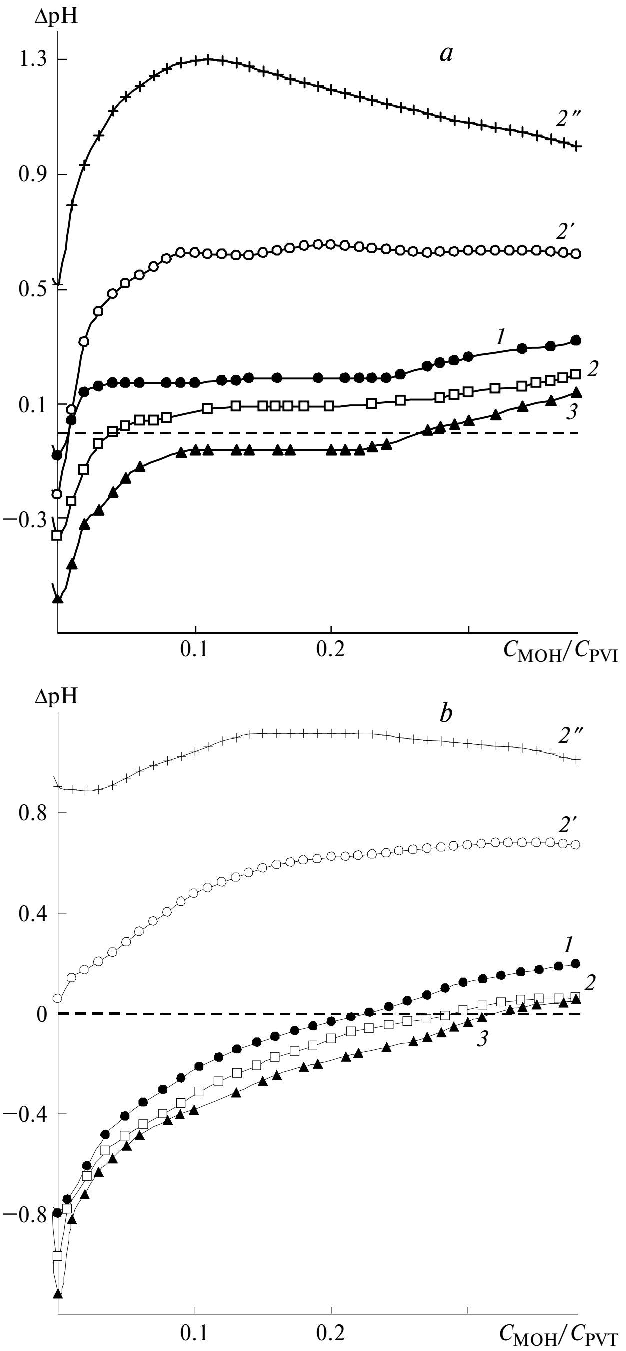


Fig. 5. Difference in the pH of a PVAz solution and water at equal concentrations of an alkali for PVI (*a*) and PVT (*b*) without salt additives (*1—3*) and in the presence of 0.1 mol L^{-1} NaCl (*2′*) and 0.1 mol L^{-1} NaBr (*2″*): LiOH (*1*); NaOH (*2*, *2′*, *2″*); and KOH (*3*).

Fig. 6. UV spectra of PVT in water at [NaOH] : [PVT] = 0 (*1*), 1 (*2*), 2 (*3*), and 5 (*4*); C_{PVT} = 0.01 mol(base) L^{-1}.

Only macromolecular substances exhibit the described changes in pH. The potentiometric titration of solutions of the low-molecular analogs (1-ethylimidazole and 1-ethyl-1,2,4-triazole) with alkalies does not show differences with a pure alkaline solution. Probably, the additional stabilization of the structures formed by the interaction of PVAz with alkalies is due to the compensation of charges by nearby adjacent units bound to the unlike ions. The parallel condensation of cations and anions on the PVAz chain results in a much lower change in the solution viscosity (see Fig. 3) during titration with an alkali than that in the systems with HCl.

The observed capability of PVAz of interacting with OH^- anions is a reason for the lowered basicity of PVI.

Coordination of the azole cycles with low-molecular cations and anions was studied by NMR and UV spectroscopy.

PVAz is characterized by multiplet signals in the ^1H and ^{13}C NMR spectra. The addition of an equimolar amount of HCl to a PVT solution shifts the signals in the ^1H NMR spectra by 0.2—0.4 ppm and in the ^{13}C NMR spectra by 1—3 ppm. In the case of PVI, the signals in the ^1H NMR spectra shift by 0.3—0.5 ppm and those in the ^{13}C NMR spectra shift by 3—7 ppm. The signals from the azole cycle are characterized by the maximum shift. When NaOH is added to solutions of PVI and PVT, the NMR spectra do not substantially change.

For the azole cycles, when the molar ratio [NaOH] : [PVT] changes from 0 to 5, the maximum of the absorption band in the UV spectrum due to the π—π^*-transition[14] shifts from ~205 to 212 nm, and its intensity decreases approximately threefold (Fig. 6). When an alkali is added to a solution of PVI, the effect of changing the band is less pronounced due to lesser withdrawing properties of the π-system of the PVI heterocycle.

Thus, we found that the azole cycles interact with acids and alkalies by different reaction centers. The protonation of the pyridine N atom of the heterocycle, resulting in a substantial redistribution of the σ-electron density, is more characteristic of PVI than of PVT. However, the interaction of the OH^- anions with the π-system is more pronounced for the triazole cycle than for the imidazole cycle.

References

1. *Polivinilazoly* [*Polyvinylazoles*], in *Entsiklopediya polimerov* [*Encyclopedia of Polymers*], Sov. Entsiklopediya, Moscow, 1974, **1**, p. 406 (in Russian).
2. C. G. Overberger and C. J. Podstadly, *Bioorgan. Chem.*, 1974, **3**, 16.
3. A. G. Lidwick and C. G. Overberger, *Rev. Roum. Chem.*, 1980, **25**, 1011.
4. M. G. Voronkov, V. A. Lopyrev, E. V. Kukharskaya, T. G. Ermakova, L. A. Tatarova, V. B. Zvyagin, and V. M. Voronkova, *Zh. Prikl. Khim.*, 1985, **58**, 190 [*J. Appl. Chem. USSR*, 1985, **58** (Engl. Transl.)].
5. Kang-Jen Liu and H. P. Gregor, *J. Phys. Chem.*, 1965, **69**, 1248.
6. M. Sakurai, T. Imai, F. Yamashita, K. Nakamura, and T. Komatsu, *Polym. J.*, 1994, **26**, 658.
7. A. A. Tager, A. P. Safronov, V. A. Lopyrev, T. G. Ermakova, L. A. Tatarova, and T. N. Kashik, *Vysokomol. Soedin.*, 1987, **29A**, 2421 [*Polym. Sci. USSR*, 1987, **29A** (Engl. Transl.)].
8. A. P. Safronov, A. A. Tager, S. V. Sharina, V. A. Lopyrev, T. G. Ermakova, L. A. Tatarova, and T. N. Kashik, *Vysokomol. Soedin.*, 1989, **31A**, 2662 [*Polym. Sci. USSR*, 1989, **31A** (Engl. Transl.)].
9. V. E. Eskin, S. Ya. Magarik, U. B. Zhuraev, and G. D. Rudkovskaya, *Vysokomol. Soedin.*, 1978, **20A**, 2219 [*Polym. Sci. USSR*, 1978, **20A** (Engl. Transl.)].
10. L. A. Tatarova, T. G. Ermakova, Al. Al. Berlin, E. F. Razvodovskii, V. A. Lopyrev, N. F. Kedrina, and N. S. Enikolopyan, *Vysokomol. Soedin.*, 1982, **24A**, 2205 [*Polym. Sci. USSR*, 1982, **24A** (Engl. Transl.)].
11. U. P. Strauss, B. W. Barbieri, and G. J. Wong, *Phys. Chem.*, 1979, **83**, 2840.
12. B. A. Bekturov and Z. Kh. Bakauova, *Sinteticheskie vodorastvorimye polimery v rastvore* [*Synthetic Water-Soluble Polymers in Solution*], Nauka, Alma-Ata, 1981, 216 pp. (in Russian).
13. N. N. Chipanina, Yu. L. Frolov, N. A. Kazakova, E. S. Domnina, and G. G. Skvortsova, *Dokl. Akad. Nauk SSSR*, 1974, **216**, 371 [*Dokl. Chem.*, 1974 (Engl. Transl.)].
14. N. N. Chipanina, N. A. Kazakova, Yu. L. Frolov, T. V. Kashik, S. M. Ponomareva, E. S. Domnina, G. G. Skvortsova, and M. G. Voronkov, *Khim. Geterotsikl. Soedin.*, 1976, **6**, 828 [*Chem. Heterocycl. Compd.*, 1976, **6** (Engl. Transl.)].

Received February 8, 2000;
in revised form July 6, 2000