

Interaction of Polydiallyldimethylammonium Salts with Iodine

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ABSTRACT: The interaction between polydiallyldimethylammonium chloride (PDADMAC) and KI or KBr, followed by changes in conformation of macromolecules, coil compaction, and counterion exchange, was detected by means of turbidimetry and viscometry. In aqueous solutions at presence of KI, PDADMAC rapidly binds iodine by the formation of polymer–iodine complexes PDADMA I[−] I_m (*m* ≤ 4). Spectrophotometric investigations of the interaction in water without KI prove the formation of complexes of polyquaternary ammonium chloride or bromide with iodine only via iodide. These ions can be generated in the polymer-catalyzed hydrolysis reaction of iodine. By inducing hydrolysis of iodine and binding the eventually formed iodide,

PDADMAC acts as an iodine acceptor with self-strengthening capacity. For the sorption of gaseous iodine, the possibility of direct interaction of its dipoles with the charged groups of the polyelectrolyte is also reasoned. Polydiallyldimethylammonium halides were used to modify activated carbon and employed in a nuclear power station for treatment of outlet gases containing radioactive iodine. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 2710–2716, 2006

Key words: polyelectrolytes; polydiallyldimethylammonium halides; iodine acceptors; self-assembly; viscosity

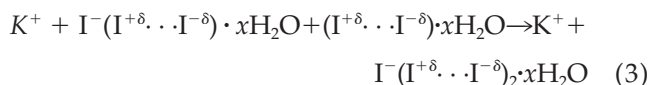
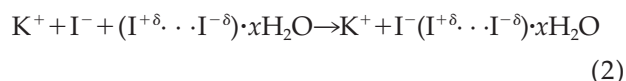
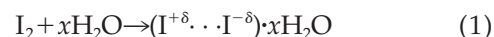
INTRODUCTION

Molecular iodine takes part in formation of colored complexes with many natural and synthetic polymers, such as starch amylose,^{1–6} polyvinylalcohol (PVA),^{1,6–11} polyvinylpyrrolidone (PVP),^{1,12–14} N-containing polymers with tertiary amino or quaternary ammonium groups,^{15–17} etc. Depending on the chemical nature of the polymers, several mechanisms of iodine binding have been proposed to explain the driving forces in this process. They include, for example, the two-stage formation of blue complexes of iodine inclusion in helix macromolecules of amylose^{2–4,6} or PVA^{6,7}; electrostatic interaction of dipoles in PVP–I₃[−] complex^{12,13}; interaction through intermediary H₂O molecules¹⁴; and direct binding via coordination bonds.¹⁸

Despite numerous well-known advances, investigations in the mentioned fields are still a matter of concern.

It is clear that iodine interacts with other compounds first of all because of a unique ability of its molecules to get polarized. This statement is particularly maintained by Mokhnach,¹ who asserts that, in water, the iodine molecule itself is a dipole (I^{+δ} . . . I^{−δ}) *n*H₂O and its electronic system can be polarized even

more in the presence of other reagents. Polarized molecules of iodine can join into chains, and in aqueous solutions of inorganic iodides, they are attached to iodide ions and form complexes of triiodide and/or pentaiodide.



It seems likely that cationic polymers containing positively charged groups would bind iodide–iodine complexes directly. The rate of interaction between these substances would be high. The fact is that for iodine extraction from geothermal water or natural mineral water bodies, ion-exchangers containing quaternary ammonium groups are applied.¹⁹ For water treatment, insoluble iodine-saturated materials with tertiary amino or quaternary ammonium groups are used as bactericides.^{15–17} In spite of the wide applications of cationic polymer–iodine complexes, no published material was found for a direct proof or denial of the aforementioned mechanism of binding iodine molecules as dipoles to these compounds. It still re-

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mains unclear whether the presence of iodide ions is crucial for the formation of iodine polycomplexes.

Ksenzenko and Stasinevich¹⁹ have established that ion-exchangers in the form of iodides are more effective iodine sorbents than those of OH⁻ or chloride. If SO₄²⁻ or CO₃²⁻ are the counterions of an anionite, they are first of all replaced by halide ions, e.g., Cl⁻, in the solution. Only thereafter, the binding of iodine to the polymer starts. The authors presented no data whether these counterions were eventually replaced by iodide ions, and have stated that iodine could be directly bound by anionites in the form of chlorides.

Polydiallyldimethylammonium chloride (PDADMAC) is a commonly used water-soluble polyelectrolyte containing quaternary ammonium groups. It is convenient to examine its interaction with iodine in low concentration solutions by means of spectrophotometry. There is no problem to replace counterions of this cationic polymer (PDADMAC) by ion-exchange reactions and to get products of different solubility in water.

This work was aimed to examine the interaction of water-soluble polyquaternary ammonium salts and iodine in different media. The results of the study would help to employ polymeric iodine complexes for use in industries, medicine, and biotechnology, as bactericides or iodine sorbents.

EXPERIMENTAL

Materials

Pure PDADMAC of different molecular weights (M_n = 15,000; 65,000, and 100,000) was purchased from Aldrich Chemicals (St. Louis, MO) in the form of 20% solutions. The super low-molecular-weight polymer sample ($M_n \sim 2000$) was obtained from Reachim (Russia) and additionally purified by precipitation in acetone–diethylether mixture (4:1) from its solution in methanol. M_n of the polymer was determined according to the published procedure.²⁰

The other polyquaternary ammonium halides such as bromide (PDADMAB), iodide (PDADMAI), and mixed salts PDADMA(Cl_{1-x}I_x) were prepared in ion-exchange reactions, as described later, by mixing PDADMAC with solutions of halides of alkali metals. The same method was applied for the preparation of PDADMA persulfate (PDADMA-PS).²¹ The concentrations of the polyelectrolytes were expressed in moles of the repeating unit per liter.

The monomer, diallyldimethylammonium chloride (DADMAC), was provided by Institute of Chemistry of Lithuania, and was not additionally purified. KI and KBr were reagents of analytical grade, obtained from Reachim.

Methods

The turbidity of the polyelectrolyte–KI mixtures was characterized by optical density, measured by a KFK-3 photocolormeter (Russia) at $\lambda = 364$ nm and $l = 1.0$ cm.

Viscometry measurements of the polyelectrolyte solutions were performed with a capillary viscometer of 0.73 mm diameter at 20°C. The measurement series were prepared from the polyelectrolyte of different M_n at its constant concentration, with changing the concentration of the various inorganic salts added.

The spectra of light absorption by polymer–iodine solutions were taken by a Specord UV–VIS spectrophotometer (Germany) in visible and UV ranges.

Gaseous iodine sorption by solid polymers proceeded in static conditions from a mixture of air and iodine vapor. Before the spectrophotometric analysis, the samples with iodine absorbed were dissolved in water. For determination of maximal iodine binding by the polymer in solutions, the amount of absorbed iodine was estimated by titrating the halide residue with sodium thiosulfate after separation of the polycomplex precipitate.

RESULTS AND DISCUSSION

In the interaction between PDADMAC and molecular iodine, the composition of iodine solutions plays an important role. To evaluate the influence of iodide ions, the interaction of PDADMAC and iodine was examined in iodine solutions, in presence and absence of KI. Another way of examination was preparation of the polymers in which Cl⁻ counterions were completely or partially substituted by I⁻ or Br⁻, and testing their binding capacity towards iodine. It is reasonable to describe these ion-exchange reactions in more detail.

The literature survey disclosed the nonspecific binding of counterions by polyelectrolytes in halide series.^{21,22} It was also corroborated for polymers with quaternary ammonium groups in the backbone of macromolecules.²² The strengthening of the polyion–counterion interaction in the series from Cl⁻ to I⁻ represented by a change in the reduced viscosity of the solutions was in reverse order to the radius of the hydrated counterion. In the case of I⁻, some polyelectrolytes became insoluble at a definite concentration of iodide. Dautzenberg et al. in the conclusions of their article²³ stated this to be true for PDADMAC in NaI solutions as well.

The behavior of PDADMAC in water solution with KI or KBr was studied by means of turbidimetry. Figure 1 shows how the turbidity of solutions depends on the concentration of inorganic salt added to the polyelectrolyte solution.

With the first portions of KI or KBr added, the PDADMAC solution becomes white, but transparency

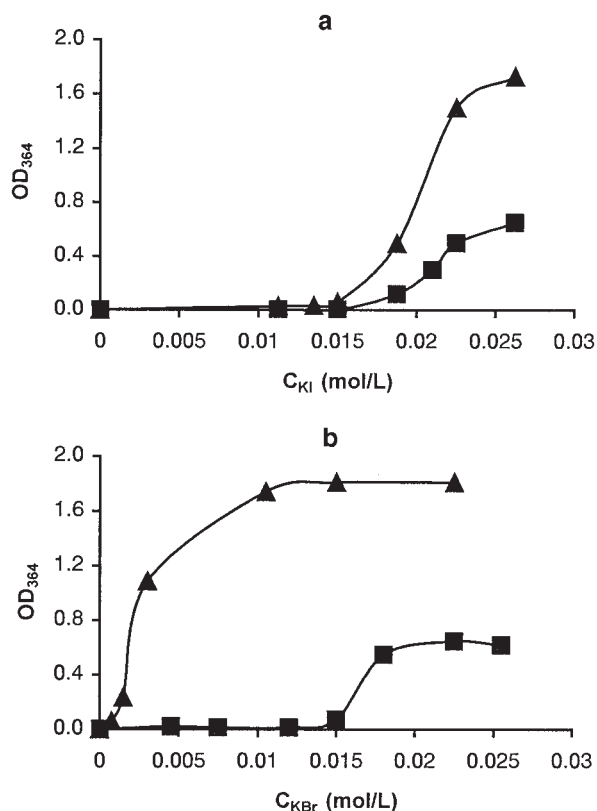


Figure 1 Dependence of turbidity of PDADMAC ($M_n = 15,000$ (■) and $M_n = 100,000$ (▲)) solutions in water (a) or water-ethanol mixtures (3:7 v/v) (b) on the nature and concentration of inorganic salts added: KI (a) and KBr (b). Concentration of the polymer was 2×10^{-3} mol/L.

returns quickly on stirring. Further, above a certain critical concentration of the inorganic salt and depending on the molecular weight of the polymer, turbidity does not disappear and increases drastically on addition of small amounts of inorganic salt. This abruptness is an indicator of a cooperative interaction. But the type of the interaction followed by a sudden formation of insoluble phase remains unclear. It might be attributed to the specific features of changes in the conformation of macromolecules during their "self-organization"; however, no abrupt change is noted in the series by viscometric measurements. Figure 2 shows how the viscosity of PDADMAC solutions changes upon addition of equivalent amounts of KCl, KBr, and KI.

The reduced viscosity of PDADMAC drops remarkably with the first portions of KI added, but further it changes uniformly. As the salt is added to the solution, coils of macromolecules are being compacted because of the screening of the similar charges of polyelectrolyte chain. For the influence on conformational changes of polymer chains (coil compacting), the inorganic salts follow this sequence: $\text{Cl}^- < \text{Br}^- < \text{I}^-$.

It is possible that the turbidimetric data presented in Figure 1 reflect also the secondary processes of inter-

molecular aggregation due to the increased hydrophobicity of the chains. Such a presumption can explain the higher values of turbidity when the long-chain polyelectrolyte is used (Fig. 1, curves of triangles).

At higher concentrations of PDADMAC and KI, a low-soluble PDADMAI precipitate is formed and can be easily separated. Chemical analysis has confirmed its composition to consist of at least 93% of Cl^- counterions substituted by I^- . Dry PDADMAI obtained from PDADMAC of the whole range of M_n studied is a pale yellowish powder, low-soluble in water at low temperatures (0.18–0.56 g/L at 18°C, 0.28–0.88 g/L at 30°C) but fairly soluble at boiling (dissolves up to 50 g/L). The solubility depends on the molecular weight of the polymer and the heating-cooling routine.

The polymer with bromine counterions can be prepared in a similar way, but with the only difference that turbidity occurs, and all procedures of separation can be performed only in water-organic solvent mixtures [Fig. 1(b)].

Interaction between PDADMAC and iodine in the presence of KI

The spectrophotometric investigation of iodine binding by PDADMAC was based on the examination of wavelength shift and change in the intensity of four characteristic bands (A, B, C and D) in light absorption spectra, identified by several authors.^{1,9–11,19} The band A ($\lambda = 226$ nm) is characteristic of aqueous solutions of iodides and is always attributed to hydrated I^- ions.^{1,9–11,19} Most authors^{9–11,19} attribute both bands B ($\lambda = 290$ nm) and C ($\lambda = 350$ nm) to the same molec-

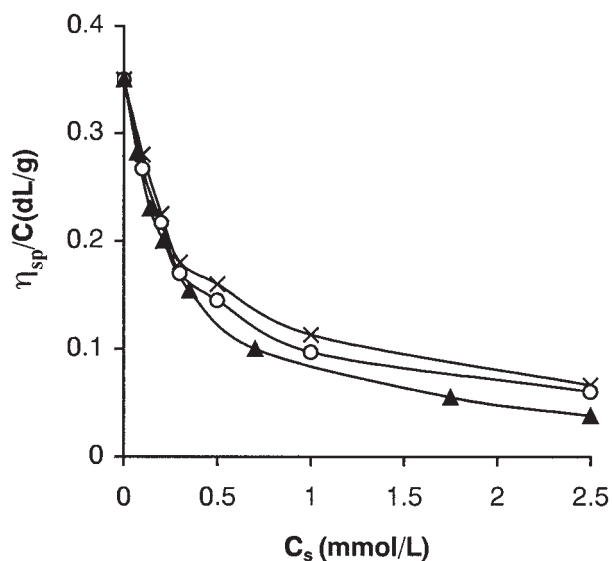


Figure 2 Variation of reduced viscosity of PDADMAC with inorganic salt concentration C_s : KCl (×), KBr (○), and KI (▲). [PDADMAC] = 1×10^{-3} mol/L, $M_n = 100,000$, and $t = 20^\circ\text{C}$.

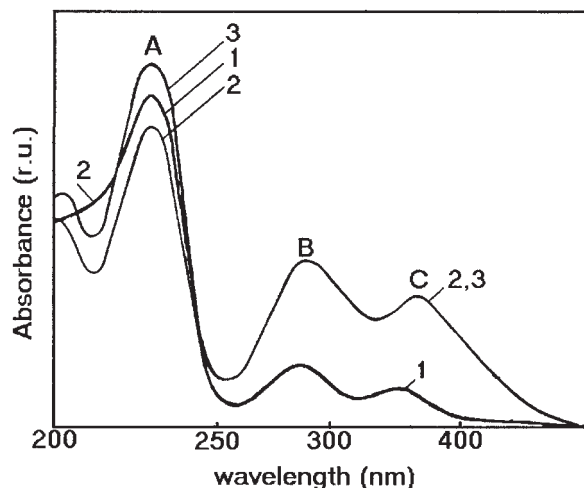


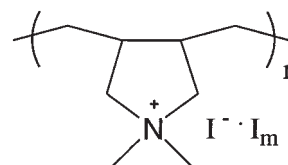
Figure 3 Light absorption spectra of KI-I_2 (1); PDADMAC and KI-I_2 (2); and PDADMAI and KI-I_2 (3). $[\text{I}_2] = 1 \times 10^{-4}$ mol/L, $[\text{I}^-] = 3 \times 10^{-4}$ mol/L, polymer concentration was 1.6×10^{-4} mol/L, $M_n = 2000$.

ular complex of triiodide ($\text{I}_3^- = \text{I}_2 \text{I}^-$). According to Yokota and Kimura,¹¹ the maximum at $\lambda = 350$ nm might be assigned to a nonlinear complex of penta-iodide $\text{I}_3^- \text{I}_2$. The absorption band D ($\lambda = 460$ nm) is admitted by all researchers to the hydrated molecules of iodine.

When polyquaternary ammonium salts, such as PDADMAC or PDADMAI, are added to the dilute solutions of iodine with KI, the yellowish brown color of the solution gets more intense and the light absorption at bands B and C increases (Fig. 3, curves 2 and 3). When the concentrations of the reagents are changed, the absorption maximums at B and C change symbatically, as if they were caused by the same derivative of iodine. Their relation is similarly changed in the $\text{I}_2\text{-KI}$ system (Fig. 3, curve 1) as well. Therefore, the maximums might be attributed to the complex of triiodide bound on the polymer chains. The difference observable when the spectrum of $\text{I}_2\text{-KI}$ with polymers and that of $\text{I}_2\text{-KI}$ alone are compared is a negligible slope at $\lambda = 400\text{--}460$ nm, i.e., in the range of D band. Since the light absorption in this range is ascribed to molecular iodine, one might suppose that polyquaternary ammonium salts bind an extra amount of molecular iodine—not only triiodide but penta-iodide as well. Chains of penta-iodide can be formed due to a higher polarization of iodine molecules in close surroundings of the polyelectrolyte macromolecules. It may be proven by a certain bathochromic shift of the C maximum in the spectra of polydiallyldimethylammonium halide— $\text{I}_2\text{-KI}$ solutions (Fig. 3, curves 2 and 3) as compared to the spectrum of $\text{I}_2\text{-KI}$ (Fig. 3, curve 1). When PDADMAC is added, light absorption at band A decreases (Fig. 3, curve 2), indicating a decrease in iodide concentration in the solution. However, the

spectra in the range of bands B and C are identical for both polymers added in equivalent concentrations. It seems reasonable to conclude that PDADMAC and PDADMAI are capable of binding the same amount of iodine from water solutions in the presence of KI in excess.

When mixing more concentrated solutions of PDADMAC and $\text{I}_2\text{-KI}$ (e.g., the concentration of I_2 is 0.1N), a rapid reaction takes place, accompanied by the formation of a fluffy brown precipitate of polymer-iodine derivatives. Analysis of the precipitate composition supplements the data of their stoichiometry. Calculation of equilibrium binding of iodine by different acceptors from $\text{I}_2\text{-KI}$ solution (Table I) shows that the cationic polymer with quaternary ammonium groups is able to bind more than 300 wt % of iodine. The binding capacity of the polymer is remarkably higher than that of its small-molecular analogue. However, the length of PDADMAC macromolecules has almost no effect on the composition of complexes of iodine and polydiallyldimethylammonium halides. Maximally, two molecules of iodine can be involved, i.e., polymeric complexes of penta-iodide are formed (Structure 1):



where $m \leq 4$. It was found that the polymeric triiodide was insoluble in water. In difference from I_3^- , it did not react with starch in water (no characteristic blue color occurred). A different interaction of polyquaternary ammonium salts with iodine was observed in aqueous iodine solutions without KI being added.

Interaction of polydiallyldimethylammonium halides with molecular iodine in water

Crystalline iodine is low-soluble in water; however, the dissolved amount is enough for spectrophotomet-

TABLE I
Values of Equilibrium Binding of Iodine from $\text{I}_2\text{-KI}$ by PDADMAC of Different Molecular Weight

Iodine acceptor	Molecular weight	Molecular iodine bound	
		equiv./equiv. of cationic groups	% ^a
PDADMAC	2,000	4.0	314
PDADMAC	15,000	4.1	321
PDADMAC	65,000	4.3	337
PDADMAC	100,000	4.3	337
DADMAC	162	1.9	148

^a The amount (in wt %) of molecular iodine bound by the polymer, when I^- weight is not taken into account.

TABLE II
Light Absorption at Bands B and C (According to Fig. 3)
by Aqueous Solutions of Various
Polydiallyldimethylammonium Halides and
Iodine after Their Interaction^a

Substance	Optical density (r. u.)	
	$\lambda = 290 \text{ nm}$	$\lambda = 360 \text{ nm}$
I ₂	0.02	0.06
PDADMAC	0.34	0.27
PDADMAB	0.32	0.25
PDADMA(Cl _{0.5} I _{0.5})	0.55	0.45
PDADMA(Cl _{0.3} I _{0.7})	0.91	0.74
PDADMAI	0.96	0.76

^a Concentration of polymers $1.5 \times 10^{-4} \text{ mol/L}$; iodine $0.5 \times 10^{-4} \text{ mol/L}$; $l = 1 \text{ cm}$.

ric measurements. These solutions contain only traces of iodide ions, because of a negligible hydrolysis of iodine.

Table II presents the data of spectrophotometric measurements when polydiallyldimethylammonium salts were added to the iodine solutions. The spectra were drawn immediately after mixing the solutions. There is an evidence of sequentially increased light absorption maximums at bands B and C by the newly prepared solutions, when Cl⁻ ions of the polymer are totally or partly substituted by Br⁻ or I⁻.

Solutions of the polymers alone do not absorb light in the considered ranges of the spectrum. Light absorption at bands B and C is most slightly increased when PDADMAC or PDADMAB are added, and it increases considerably with the addition of PDADMAI. Solutions of mixed polyelectrolyte salts and iodine are in the middle at this point of view. According to the data of the investigations, the conclusion can be drawn that the binding capacity of PDADMAI towards iodine is the greatest among the polymers presented in Table II.

The remarkable property of polyquaternary ammonium iodide to form polymer complexes with iodine might be explained by a peculiar structure and conformation of its macromolecules. However, as Figure 2 reveals, an exceptional role of iodide in iodine binding might not be explained only by a decrease in hydrodynamic volume of the coils. Most likely, in the formation of the contact ion pairs polymer (N⁺(R)₃I⁻) the internal orientation of the chains is switched, and in this way, the macromolecules of the polyelectrolytes get "adjusted" for binding of molecular iodine.

When the solution of PDADMAC and iodine was left at room temperature for a longer period of time, the absorption at band A became more intense, while the absorption maximums at B and C diminished (Fig. 4). The intersecting lines of the spectra have two isobestic points at $\lambda = 212$ and 241 nm . It is an evidence of iodide ions occurring in the system of poly-

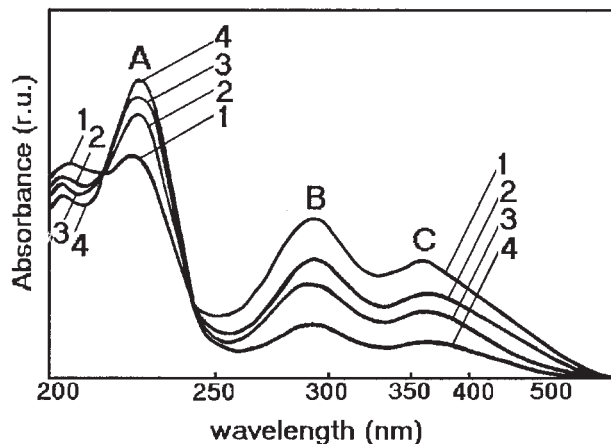
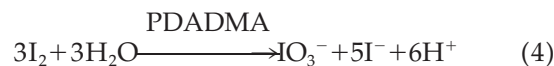


Figure 4 Changes in light absorption spectrum of PDADMAC-iodine aqueous solutions in time: 1, fresh solution; 2, after 4 h; 3, after 6 h; 4, after 24 h; $[I_2]_{\text{initial}} = 0.6 \times 10^{-4} \text{ mol/L}$, $[PDADMAC] = 3 \times 10^{-4} \text{ mol/L}$.

mer-iodine. After 2 days, the solutions were almost discolored; light absorption at bands B and C was decreased to the minimum. Such changes in the spectra might be explained in terms of hydrolysis of iodine molecules polarized in close neighborhood of PDADMAC macromolecules¹⁹:



It is supported by changes in pH of PDADMAC and iodine aqueous solutions. During iodine hydrolysis according to eq. (4), iodine acids of two kinds are formed, and H⁺ concentration in solutions is increased. Data presented in Figure 5 show the acceleration of molecular iodine hydrolysis by some cationic polyelectrolytes. The pH of aqueous solutions of

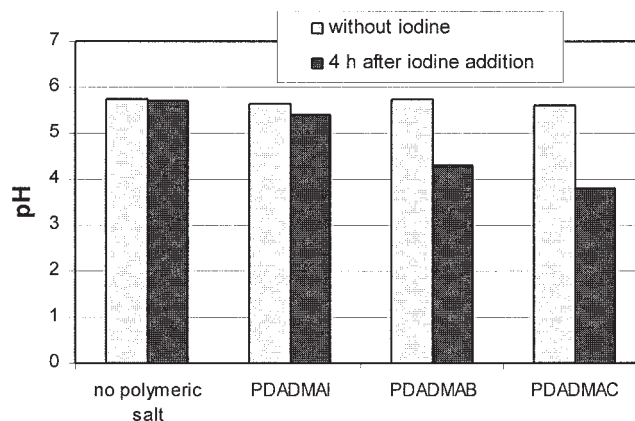


Figure 5 Changes in pH of aqueous solutions of the polymeric salts ($C = 5 \times 10^{-3} \text{ mol/L}$) with the addition of iodine at the dose of $0.75 \times 10^{-3} \text{ mol/L}$.

TABLE III
Values of Gaseous Iodine Sorption by Polyquaternary Ammonium Salts^a

Substance	Amount of iodine sorbed (g/g of sorbent)
PDADMAI	1.85
PDADMAC	0.66
PDADMA-PS	0.21

^a Sorption proceeded for 72 h; iodine concentration in the atmosphere was about 0.003 g/L.

PDADMAC, PDADMAB, PDADMAI, as well as I₂, is quite similar and changes in time insignificantly. With the addition of I₂ to aqueous solutions of the polymeric salts, pronounced differences in pH changes are observed. The pH of PDADMAI decreases very slightly, while in the case on PDADMAB and PDADMAC, the pH value drops remarkably already at the initial moment and still decreases a little afterwards. After 4 h, the pH of PDADMAC-I₂ and PDADMAB-I₂ solutions is 3.8 and 4.3, respectively, and the same of PDADMAI is 5.4. The higher decrease in pH in the solutions of PDADMAC and PDADMAB might be explained as a shift to the products of the reaction according to eq. (4) because of I⁻ binding by these polycations.

With the occurrence of I⁻ in the solution, as shown earlier, the polyelectrolyte gets able to bind higher quantities of molecular iodine, which is eventually producing new iodide ions. During this process, the acceptory ability of PDADMAC as an I₂ sorbent gradually increases, as PDADMAC is transformed to PDADMAI. The latter is the best iodine acceptor among all the polyquaternary ammonium halides. Therefore, PDADMAC promoting hydrolysis of iodine acts as a self-strengthening acceptor of iodine. Iodine affinity to this polymeric mixed salt increases, until the amount of iodide becomes equivalent to quaternary ammonium groups of the polymer. Such a process of self-strengthening is very important for their application in various technologies.

Sorption of gaseous iodine by solid polydiallyldimethylammonium salts

Iodide salts of the polymers manifest themselves also as sorbents of gaseous iodine. Three polymeric salts, PDADMAI, PDADMAC, and PDADMA-PS, were crushed to powder and exposed for 72 h in the atmosphere of gaseous iodine. Comparative data on iodine sorption are given in Table III.

Hydrolysis of iodine leading to I⁻ formation is feebly probable on the chains of PDADMAC at low humidity of air and totally impossible in the case of PDADMA-PS because of the oxidizing behavior of the latter. In spite of this, small amounts of iodine were attached to PDADMAC and certain negligible quanti-

ties to PDADMA-PS, probably because of a direct interaction of iodine molecules as dipoles with the highly polar groups of the polymers. This assumption is well supported by a spectrophotometric investigation of aqueous solutions of PDADMAC, preexposed in solid state to iodine vapor for a short time (Fig. 6, curve 2). Its spectrum is different from that presented in Figure 3 and has the better-pronounced inflection point at $\lambda = 460$ nm (band D), which is specific for molecular iodine (Fig. 6, curve 1). It is possible that the ion-dipole interaction occurs distinctly only for polyelectrolytes in solid state when the macromolecules are drawn closer to each other. In water, similar rearrangement takes place due to the chain-shrinking action of I⁻ ions.

PDADMAI, as expected, has been found able to bind the largest amount of gaseous iodine in the same conditions. Bearing in mind the possibility to treat various surfaces, including activated carbons, by hot solutions and an extremely high sorption capacity of the polymer towards iodine, it offers a good alternative for insoluble ion-exchangers.

PDADMAI obtained in ion-exchange reaction from PDADMAC and inorganic iodide salts in mixture with PDADMAC was immobilized in granulated activated carbon. The carbon modified in such a way is a strong acceptor of iodine. It was employed in a nuclear power station for treatment of outlet gases containing radioactive iodine. The binding of radioactive iodine by such sorbents was as efficient as that of chemical acceptor of iodine, AgNO₃.

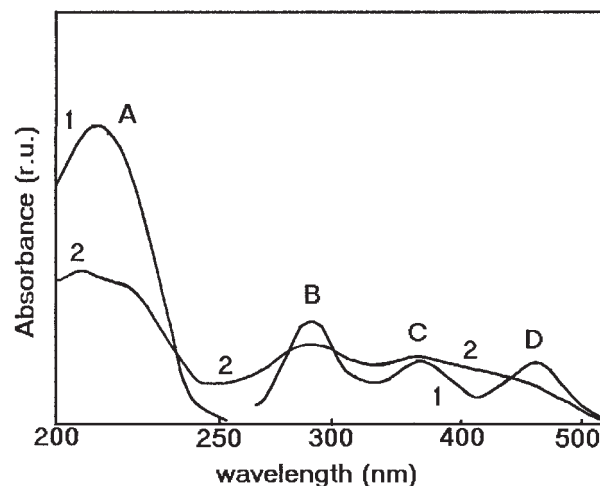


Figure 6 Light absorption spectrum of the solution of PDADMAC preexposed to gaseous I₂ (2) compared to the spectrum of I₂ aqueous solution (1).

CONCLUSIONS

PDADMAC interacts cooperatively with KI or KBr in ion-exchange reaction followed by changes in confor-

mation of macromolecules and coil compaction. In aqueous solutions of PDADMAC with iodine at presence of KI, polymer complex PDADMA I⁻ I_m ($m \leq 4$) is formed. In iodine aqueous solution without KI, polyquaternary ammonium chloride or bromide bind iodine only due to formation of iodide, which can be generated in the polymer-catalyzed hydrolysis reaction of iodine. By inducing hydrolysis of iodine and binding the eventually formed iodide, PDADMAC acts as an iodine acceptor with self-strengthening capacity. For the sorption of gaseous iodine, the possibility of direct interaction of its dipoles with the charged groups of the polyelectrolyte is also reasoned.

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