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FEATURES OF LONGITUDINAL FLOW OF SOLUTIONS OF HYDROLYZED POLYACRYLAMIDE CONTAINING SULFUR MICROPARTICLES

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Abstract. The features of the flow of solutions of nonionic and hydrolyzed polyacrylamide (18%) in the presence of sulfur microparticles on a VK viscometer were studied. It was determined that in a submerged jet of solutions (≤ 5 cm^3/s) the orientation factor of macromolecules reaches ≤ 0.8. The transformation of a free jet (≥ 8 cm^3/s) into an aerosol of flocculated sulfur microparticles was revealed.

Keywords: polyacrylamide, hydrolyze, sulfur, microparticles, jet, aerosol, flocculant.

Гидролизланган полиакриламиднинг олтингугурт микрозаррачалари тутган эритмаларини бўйлама оқими хусусиятлари

Аннотация. Ноионоген ва гидролизланган полиакриамид (18 %) эритмаларининг олтингугурт микрозаррачалар иштирокида оқишдаги хусусиятлари ВК вискозиметрида ўрганилган. Чўктирилган оқимда (≤ 5 $см^3$/с) макромолекулалар ориентация фактори ≤ 0,8 га эришиши аниқланган. Эркин оқимни (≥ 8 $см^3$/с) флокулланган олтингугурт микрозаррачали аэрозолга айланиши аниқланган.

Калит сўзлар: полиакриаламид, гидролиз, олтингугурт, микрозаррача, оқим, аэрозоль, флокуллиант.

Особенности продольного течения растворов гидролизованного полиакриламида, содержащих микрочастиц серы

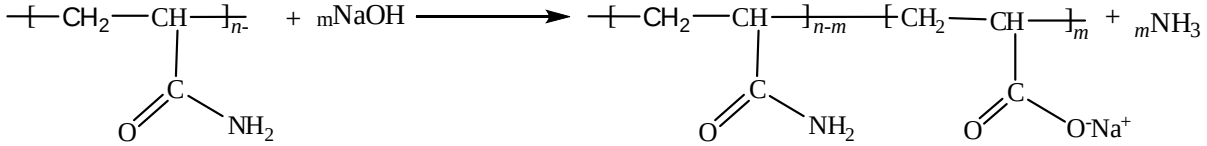
Аннотация. Изучено особенности течения растворов неионогенного и гидролизованного полиакриламида (18 %) в присутствии микрочастиц серы на вискозиметре ВК. Определено, что в затопленной струе растворов (≤ 5 $см^3$/с) фактор ориентации макромолекул достигает ≤ 0,8. Выявлено превращение свободной струе (≥ 8 $см^3$/с) в аэрозоль флокулированных микрочастиц серы.

Ключевые слова: полиакриаламид, гидролиз, сера, микрочастица, струя, аэрозоль, флокуллиант.

Introduction

Samples of polyacrylamide (PAA) and its ionic (anionic and cationic) derivatives are characterized by a high molecular weight (> 10^6), flexibility and water solubility, which makes it possible to use them as chain compounds effectively interacting with various elements, particles in the form of binders, flocculants, stabilizers, structurants, thickeners, dispersants, carriers and the like [1-3].

Ionic derivatives can be obtained by hydrolysis of polyacrylamide (HPAA), for example, by selecting the conditions for the action of alkali NaOH, anionic derivatives with different degrees of hydrolysis (DH) are obtained. Partly hydrolyzed PAA molecules (DH <20%), in which amine groups (NH_2) in separate elementary units are converted to carbosilate (ONa) groups, and ammonia compounds (NH_3) are isolated as a by-product [4]:



The formation of an ionic carboxylate group is accompanied by an increase in the molecular weight of the polymer sample and the appearance of a polyelectrolyte effect in solutions, which can be controlled on depending on the DH. Very long ionic molecules of partially hydrolyzed polyacrylamide do not lose the molecular flexibility characteristic of the initial PAA. They effectively flocculate suspended dispersed micro- or nanosized particles in solutions. In this case, particles can be simultaneously fixed by several types of interactions, in particular, van der Waals, hydrogen, ionic, etc. This increases the strength and retention time of the particles by macromolecules, i.e. prolongation effects are observed, which depend on DH [5]. The latter is very important for reducing the processes of disintegration and sublimation of particles. Especially when the solution is applied to the surface and converted into a composite with particles. In this, it is important to use the flocculating ability of macromolecules to increase the prolongation time of particles, for example, bioactive micro particles of sulfur, which are of interest as

insecticides against insects, plant pests and sanitary and hygienic preparations in warehouses [6, 7]. An important task is to apply the solution in the form of an aerosol according to the principle of a spray gun and to achieve a high degree of adhesion on the surface. The present work was carried out in this aspect, in which the molecular weight characteristics of partially hydrolyzed polyacrylamide, the orientation-deformation behavior of macromolecules in a submerged stream of a longitudinal field, and the "jet - aerosol" transformation in a free jet. As well as the possibility of samples PAA and HPAA as a flocculants-fixer of sulfur micro particles with an adjustable prolongation property.

Objects and methods

Nonionic PAA produced at Navoiazot JSC (Uzbekistan) and its partially hydrolyzed HPAA sample with DH = 18%, as well as sulfur micro particles with an average size of 5 microns, obtained by mechanical grinding of a purified finely dispersed product isolated during processing natural gas at the Mubarek plant (Uzbekistan). The study was carried out for aqueous solutions of PAA and HPAA, their mixtures with micro particles of sulfur. The molecular weights (M) of the polymers were determined by the hydrodynamic method of Ubbelode viscometry (VU). The structural and phase transformations of the mixtures were investigated in a submerged and free jet using the rheological method of Kuvshinsky viscometry (VK) and rheological method [8-10].

Results and its discussion

The hydrolysis was carried out for 50 ml of an aqueous solution of PAA with a concentration of C = 1 g/dl under the action of 2.5 ml of an alkaline solution of 5 M NaOH at 50 °C for 1 hour. As a result we obtained partially hydrolyzed polyacrylamide with a degree of hydrolysis of 18%, which was determined by potentiometric titration according to [2, 11].

To determine the molecular weight of PAA and HPAA the viscosity parameters were measured upon dilution by the Ubbelode viscometry method at 25 °C [12]. Based on the data obtained the dependence of the reduced viscosity (η_{sp}/C) on the concentration (C) was constructed according to the Huggins law $\eta_{sp}/C = [\eta] + k[\eta]^2C$ (where k is the coefficient) shown in Fig.1. In order to suppress the polyelectrolyte effect, NaCl (2%) was added to the HPAA solution. By extrapolating $C \rightarrow 0$ the value of intrinsic viscosity $\eta_{sp}/C = [\eta]$ was found, which turned out to be equal to $[\eta]$ = 10.5 dl/g for PAA and $[\eta]^*$ = 14.8 dl/g for HPAA. According to [8], the value of the molecular weight (M) of the samples was calculated using the Mark-Kuhn-Houwink equation: $M = ([\eta]/6.31 \times 10^{-5})^{1/0.8} = 3361000$ for PAA and $M^* = ([\eta]^*/6.15 \times 10^{-5})^{1/0.82} = 3675000$ for HPAA. A sample of finely dispersed sulfur was purified and ground additionally in a ball mill, fractionated through a sieve system, and microparticles with an average size of about 5 mkm were taken. It should be noted that sulfur particles less than 20 mkm in size are used in agriculture for pest control and in medicine as anti-inflammatory and disinfectants. In this aspect, there is a problem with the retention of the sulfur particles after application to the surface, since they easily disintegrate and sublimate due to the very low adhesion. In principle, it is possible to increase adhesion by means of polyacrylamide flocculants adhering to suspended particles in solutions, retaining them when the solution is applied to the surface as a thin layer or coating with flocculated aerosol particles. In such cases, an extension of the period of action (prolongation) of sulfur particles is provided, screening their scattering and sublimation.

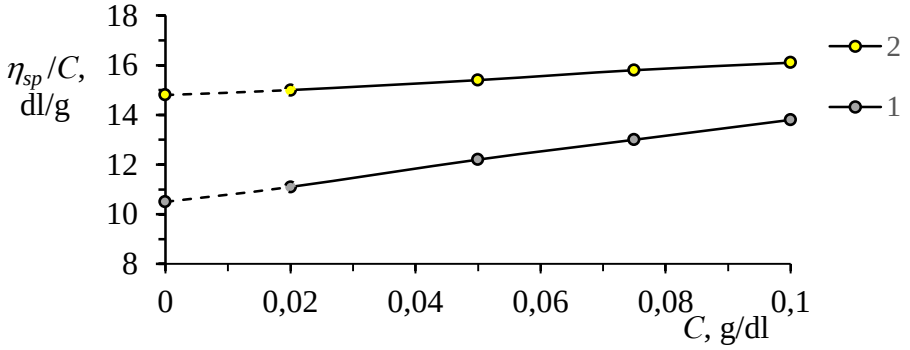
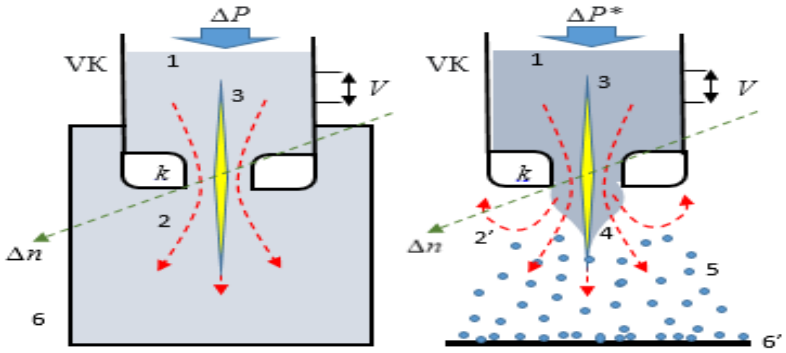


Fig. 1. Dependence of reduced viscosity (η_{sp}/C) on concentration (C) for PAA solutions in water (1) and HPAA in 0.2% NaCl + water (2) at 25 °C.

In this, it is important to study the rheological behavior of polyacrylamide solutions in the presence of sulfur microparticles in the flow, namely, structural changes in macromolecules and phase transformations of mixtures in the modes of a submerged and free jet [8-10]. Such studies were carried out on a Kuvshinsky short-capillary viscometer in a wide range of shear stress, i.e. external influence of air pressure (ΔP) (Fig. 2). In the zone of the short capillary VC, a longitudinal field is formed and a non-Newtonian flow of the solution (or mixture) is realized, which characterizes the effective viscosity η_{eff} =

$k\Delta Pt$. Here k = 10.02 is the constant of the short capillary, t is the time of the solution (mixture) outflow with the volume V. The intensity of the flow is estimated from the volumetric flow rate $Q = V/t$. In the submerged jet regime, an oriented - deformational ordering of macromolecules occurs in a realized longitudinal field (Fig.2a). In this case, the behavior of macromolecules strongly depends on the degree of flocculation of particles. In the free jet mode at the outlet of the capillary, the formed unstable Taylor cone of the solution (or mixture) quite abruptly turns into a turbulent flow of aerosol (or hydrosol) when high pressure is supplied ($\Delta P^* >> \Delta P$) to the VK (Fig. 2 b).



a b

Fig. 2. Schematic representation of the implementation of a submerged jet (a) and a free jet (b): 1 - solution; 2 - streamlines of laminar flow; 2 '- streamlines of turbulent flow; 3 - anisotropic phase of oriented macromolecules; 4 - Taylor cone; 5 - aerosol particles; 6 - solution reservoir; 6'- platform for receiving flocculated particles; Δn is the birefringence in the anisotropic region.

Rheological experiments were carried out for dilute aqueous solutions of PAA and HPAA satisfying the conditions of non-overlap of macromolecules according to the criterion $[\eta]C$ <1. Microparticles of sulfur were added to the solutions by weight equal to the weight of the polymer, i.e. PAA:S:water = 1:1:100 and HPAA:S:water = 1:1:100. Since sulfur does not dissolve in water, its microparticles behave like suspended particles in solutions. Such systems can be considered as a mixture of polymers with microparticles or suspensions. In general, for these systems, it is important to identify the difference in the course of flocculation of microparticles as a consequence of thermodynamic and rheological factors.

Thermodynamic factors, in principle, are based on the structural and functional abilities of macromolecules for flocculation of microparticles and are implemented for a long time without the influence of external forces. To assess the course of such flocculation, the prepared mixtures were kept for more than a day without any external influences. The results showed bleaching of the mixtures due to the deposition of flocculated particles. Comparative IR spectroscopic data showed mixing of the absorption band in the case of a mixture in the region of wavenumbers of 1600 cm^{-1}, 1250 cm^{-1}, and 1100 cm^{-1} [13]. This indicated the occurrence of flocculation as a result of intense interaction of macromolecules with microparticles.

Rheological factors are mainly based on the implementation of the transition of macromolecules to an unfolded and oriented state in a longitudinal field generated in the submerged jet mode and thereby achieving high degrees of interactions of unfolded functionally active macromolecules with microparticles in a gradient flow. Also, the implementation of the transformation "jet - aerosol" in a free jet and the application of flocculated microparticles of sulfur on the surface with controlled prolongation.

The results obtained in the flow of a submerged jet are presented in Fig. 3 in the form of the dependence of the effective viscosity (η_{eff}) of the volumetric flow rate (Q) of solutions of polyacrylamide samples and their mixtures with sulfur microparticles. In this range of Q, a laminar flow of samples of solutions and mixtures is realized. There is a Newtonian flow characteristic of the orientational - deformational ordering of macromolecules in the range of $Q \leq 5$ cm^3/s. In this case, the polarization optical observation showed the manifestation of optical anisotropy in a wide range of Q, and in the region of $Q > 5$ cm^3/s, when the flow becomes Newtonian (established), the orientation factor of macromolecules (β) is achieved $\beta = \Delta n/\Delta n_o$ = 0.6 - 0.8. Here, Δn is the fluid and Δn_o is the limiting value of birefringence in the anisotropic region of the longitudinal field [14]. This value of β indicates the achievement of a high degree of orientation of macromolecules in the submerged jet.

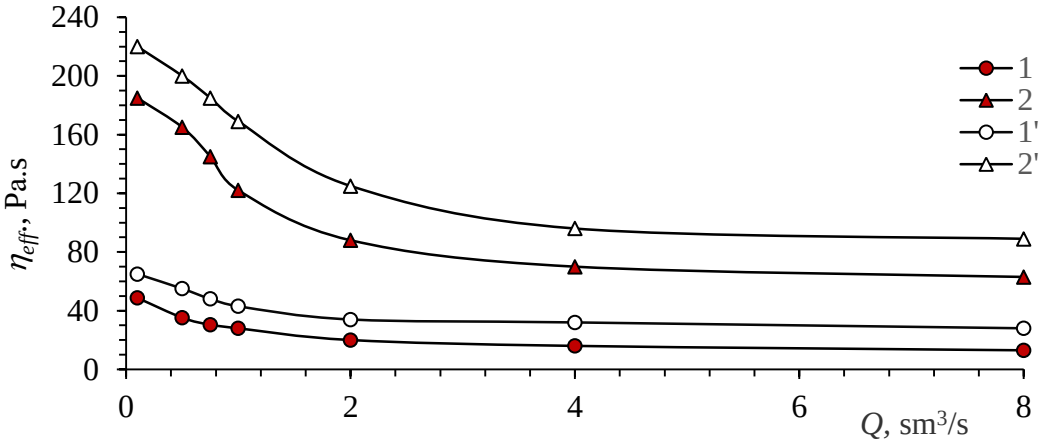


Fig. 3. Dependence of the effective viscosity (η_{eff}) on the volumetric flow rate (Q) with a flooded jet of PAA (1) and HPAA (2) solutions, PAA: S (1 ') and PAA: S (2') mixtures.

All other things being equal, by replacing the reservoir with a platform at the VK, the transition from the submerged jet mode to the free jet mode is carried out (see Fig. 2). Since, in both modes, the viscous and anisotropic indicators are measured at the inlet zone of the inner part of the short VK capillary, the results obtained will be very close. The difference is observed outside the capillary when the action of the longitudinal field is excluded. In the case of a submerged jet, the anisotropic phase in solution is retained for some time due to the duration of the relaxation period of folding of oriented macromolecules. In the case of a free jet outside the capillary, a solution Taylor's cone is formed, the stability of which in air largely depends on the surface tension (α) of the solution. The anisotropic phase in the cone is preserved as in a submerged jet at the same range of ΔP and Q, providing a laminar flow. At large $\Delta P^* > \Delta P$ and $Q^* > Q$, the surface tension becomes insufficient to hold the Taylor cone, i.e. the cone collapses and a turbulent flow is realized, leading to the "jet - aerosol" transformation. The results of such studies, carried out in the free jet mode for polyacrylamide solutions and mixtures with sulfur, are shown in Fig. 4 in the form of the dependence of the effective viscosity (η_{eff}) on the volumetric flow rate (Q).

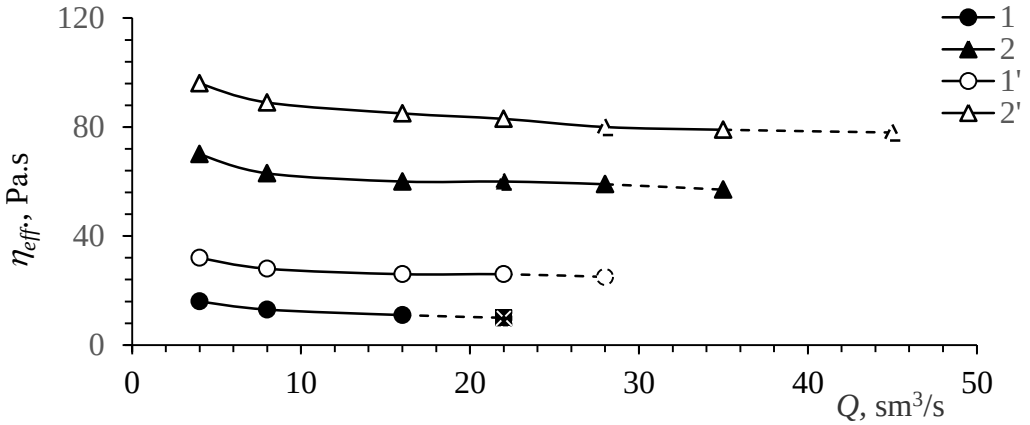


Fig. 4. Dependence of the effective viscosity (η_{eff}) on the volumetric flow rate (Q) for a free jet of PAA (1) and HPAA (2) solutions, PAA:S (1') and PAA:S (2') mixtures.

It can be seen from the graphs that the curves are mixed in the region of large values of the effective viscosity due to the difference in the molecular weight of the samples and in the content of sulfur microparticles, as well as an increase in Q. In the graphs of dependencies, there are characteristic points Q^*, after which dashed lines represent the lines of the curves. Moreover, such values $Q^* \geq 16$ cm^3/s for PAA, $Q^* \geq 28$ cm^3/s for HPAA, in the case of sulfur content $Q^* \geq 22$ cm^3/s for PAA:S and $Q^* \geq 36$ cm^3/s for HPAA:S. Points Q after the dotted line characterize the limiting value of the volumetric flow, behind which the Taylor cone in the outlet zone is practically not formed. The “jet - aerosol” transformation begins at the outlet of the capillary and continues to the platform, on the surface of which aerosol particles accumulate in the form of a coating.

Comparative analysis showed that after the application of aqueous suspensions of microparticles without the participation of polyacrylamide samples on the surface of the platform, the prolongation period,

i.e. disintegration and sublimation time lasted 5 - 7 days. When flocculated sulfur microparticles are applied with polyacrylamide samples, the prolongation period is increased by more than two months. This shows the high efficiency of polyacrylamide samples as a flocculant-fixer of sulfur microparticles on the surface.

Thus, research results have shown that behavior of polyacrylamide solutions and mixtures with sulfur microparticles in the flow regimes of a submerged jet and a free jet of longitudinal field largely depends on the molecular weight, the degree of hydrolysis, the presence of sulfur microparticles in the solutions and their flocculation with the selected polymers in the presence and absence. It was revealed that polyacrylamide molecules pass a high degree of orientation state and effectively come into contact with sulfur microparticles. The use of PAA and HPAA samples increases the prolongation of the disintegration and sublimation of sulfur microparticles on the surface, which can be adjusted by a set of molecular structural characteristics of polymers and the mode of application of flocculated particles on the surface in the form of an aerosol.

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MUALLIFLAR DIQQATIGA!

Hurmatli mualliflar, maqola muallif tomonidan qog‘ozda chop etilgan va elektron shaklida taqdim qilinishi shart. **Maqolada quyidagi bandlar**: UDK, ishning nomi (o‘zbek, rus va ingliz tillarida), maqola hammualliflarining ro‘yxati (to‘liq familiyasi, ismi, otasining ismi – o‘zbek, rus va ingliz tillarida), muallif haqida ma’lumotlar: ish joyi, lavozimi, pochta va elektron pochta manzili; maqola annotatsiyasi (300 belgigacha, o‘zbek, rus va ingliz tillarida), kalit so‘zlar (5-7, o‘zbek, rus va ingliz tillarida) bo‘lishi lozim.

MAQOLALARGA QO‘YILADIGAN TALABLAR!

Maqolalarning nashr etilishi uchun shartlar nashr etilishi mo‘ljallangan maqolalar dolzarb mavzuga bag‘ishlangan, ilmiy yangilikka ega, muammoning qo‘yilishi, muallif tomonidan olingan asosiy ilmiy natijalar, xulosalar kabi bandlardan iborat bo‘lishi lozim; ilmiy maqolaning mavzusi informativ bo‘lib, mumkin qadar qisqa so‘zlar bilan ifodalangan bo‘lishi kerak va unda umumiy qabul qilingan qisqartirishlardan foydalanish mumkin; “Ilmiy axborotnoma” jurnali mustaqil (ichki) taqrizlashni amalga oshiradi.

MAQOLALARNI YOZISH VA RASMIYLASHTIRISHDA QUYIDAGI QOIDALARGA RIOYA QILISH LOZIM:

Maqolalarning tarkibiy qismlariga: kirish (qisqacha), tadqiqot maqsadi, tadqiqotning usuli va obyekti, tadqiqot natijalari va ularning muhokamasi, xulosalar yoki xotima, bibliografik ro‘yxat. Maqola kompyuterda Microsoft Office Word dasturida yagona fayl ko‘rinishida terilgan bo‘lishi zarur. Maqolaning hajmi jadvallar, sxemalar, rasmlar va adabiyotlar ro‘yxati bilan birgalikda doktorantlar uchun 0,25 b.t. dan kam bo‘lmasligi kerak. Sahifaning yuqori va pastki tomonidan, chap va o‘ng tomonlaridan - 2,5 sm; oriyentatsiyasi - kitob shaklida. Shrift - Times New Roman, o‘lchami - 12 kegl, qatorlar orasi intervali - 1,0; bo‘g‘in ko‘chirish - avtomatik. Grafiklar va diagrammalar qurishda Microsoft Office Excel dasturidan foydalanish lozim. Matndagi bibliografik havolalar (ssilka) kvadrat qavsda ro‘yxatda keltirilgan tartibda qayd qilish lozim. Maqolada foydalanilgan adabiyotlar ro‘yxati keltirilishi lozim. Bibliografik ro‘yxat alfavit tartibida - GOST R 7.0.5 2008 talablariga mos tuziladi.

- Ikki oyda bir marta chiqadi.
- “Samarqand davlat universiteti ilmiy axborotnomasi”dan ko‘chirib bosish faqat tahririyatning yozma roziligi bilan amalga oshiriladi.
- Mualliflar maqolalardagi fakt va raqamlarning haqqoniyligiga shaxsan mas’ul.

MAQOLAGA QUYIDAGILAR ILOVA QILINADI:

- Yo‘llanma xati;
- Ekspert xulosasi.

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