



---

Soviet-era science, translated into English

# Chemistry

S. A. Glikman, Corresponding Member of the Academy of Sciences  
of the USSR S. N. Ushakov,

1964

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196401.36326>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

## Abstract

## Full Text

### *Chemistry*

S. A. Glikman, Corresponding Member of the Academy of Sciences of the USSR  
S. N. Ushakov,  
E. P. Korchagina, E. N. Lavrent'eva

## On Some Properties of Iodine-Polyvinyl Alcohol Gels

Thixotropic gels of iodine-polyvinyl alcohol (IPVA) were first described by one of us <sup>(1)</sup>. "Filled" gels, which received the conventional name of "two-phase" IPVA gels, have also been described <sup>(2)</sup>.

Thixotropic IPVA gels are obtained <sup>(3)</sup> by first preparing aqueous PVA solutions and then adding solutions of iodine in an aqueous solution of potassium iodide and agents that ensure the formation of labile "cross-links" between the chain macromolecules of PVA. Such agents include various boron derivatives (borax, boric acid, etc.), as well as dyes of the Congo red type, benzopurpurine derivatives, and others. Gel formation occurs upon gradual cooling of the mixture of the indicated ingredients, previously heated to the temperature at which the iodine-PVA complex compound, colored blue, decomposes. The gelation temperature of the mixture depends on the concentration of the solution and the molecular weight of the PVA, the amount of iodine and cross-linking additives introduced into the mixture, and can be regulated accordingly.

In two-phase IPVA gels, in order to increase the concentration of PVA and iodine while maintaining the gelation temperature and the viscosity of the melt, dispersed powders of iodine complexes of cross-linked copolymers of vinyl alcohol are introduced into the solution; these powders are incapable of dissolving or swelling in water or in solutions that form IPVA gels <sup>(4)</sup>. Such powders are obtained by copolymerizing vinyl acetate or other complex vinyl esters with tetrareactive monomers (diallyl acetals, methylenecrotonamide diesters, etc.), followed by saponification of the copolymers in a heterogeneous medium, or by reactions between polyvinyl alcohol chains leading to the formation of bridging bonds <sup>(5)</sup>. Iodine complexes of such powders may be obtained by the method of heterogeneous reaction with iodine solutions <sup>(6)</sup>.

Study of the possibility of practical use of IPVA gels <sup>(7)</sup> revealed the need for an exact physicochemical characterization of their properties and of the dependence of these properties on a number of factors.

Since the basis of the gels is a polymer whose molecules are heterogeneous in structure and chemical composition, it is necessary to study the influence on the properties of the gels of the features of these molecules, in particular the

average degree of polymerization, molecular-weight distribution, branching of the molecules, and the quantitative content in them of residual acetyl groups, 1-2 glycol groups, and metal ions. All these factors primarily determine the properties of PVA solutions from which IPVA gels are obtained.

It is known that aqueous PVA solutions are not true solutions. Their viscosity changes with time as a result of structuring due to the separation, in the form of a second phase, of fractions insoluble in the given medium and at the given temperature; in some cases this leads to general gelation of the entire aqueous solution without the introduction of additional components.

The study of changes with time in the viscosity and light scattering of aqueous PVA solutions that differ from one another in molecular weight, in

content of residual acetate groups and by solubility showed that the aging processes of solutions of these samples proceed quite differently.

It was also established that the introduction into them of additions of monohydric alcohols of the fatty series (in particular, 10% ethyl alcohol) strongly weakens the aging processes of any PVA sample, and the effect of the additions increases with increasing molecular weight.

Two methods were used to separate a PVA sample into fractions: 1) successive extraction with a water-acetone mixture at increasing temperatures and 2) the recently proposed method for polystyrene<sup>(8)</sup>, somewhat modified by us, of slow freezing of the solution. The results obtained were in general analogous; moreover, the freezing method, being simpler and faster, leads to a greater distinction between the fractions in molecular weight and to a smaller distinction in acetyl numbers.

The gelation temperature of IPVA solutions was determined viscometrically with an accuracy of  $\pm 0.5^\circ$ . The lowest temperature at which the viscosity of the solution does not increase over the course of three hours was taken as the temperature threshold of gelation. To measure the viscosity of dark IPVA solutions we used a modified Höppler viscometer, in which registration is carried out on the principle of measuring the inductive resistance at the moment of passage of a steel ball, which is indicated by a signal lamp or by automatic starting of a stopwatch.

It was found that an increase in the iodine content in IPVA solutions leads to a significant increase in the gelation thresholds (for example, for 6% solutions from  $35.5^\circ$  at 9% iodine to  $39.5^\circ$  at 15% iodine). The content of boric acid also plays a role; for example,  $36.5^\circ$  without boric acid,  $37.5^\circ$  at 2%,  $38.5^\circ$  at 4%, and  $41.5^\circ$  at 6% boric acid.

To determine the viscoelastic constants of gels, the method of tangential displacement of a plate was used<sup>(9)</sup>. The data obtained show that, in comparison with other polymers, IPVA gels are characterized by high elasticity at relatively low relaxation viscosity.

The introduction of boric acid in an amount of 2% relative to PVA has a comparatively small strengthening effect on 6% IPVA gels (containing 9% iodine). The introduction of 6% boric acid, however, leads to a 10-fold increase in  $P_k$  of the gels.

Increasing the iodine content in the gels from 9 to 15% (with a boric acid content of 2%) leads to an increase in  $E_1$  by almost 7 times, and in  $P_k$  by 14 times. All the investigated gels noticeably age after two or three days (especially gels containing 15% iodine).

The properties of the gels depend to a considerable extent on the thermal treatment of the initial solutions, in particular on the time of additional heating after the mixing, carried out at 70°, of the PVA solution with a solution of iodine in KJ added dropwise.

In this connection, it is of interest to study the nature of the interactions of PVA with iodine and KJ in aqueous solutions, carried out by the spectrophotometric method.

Studies of this kind <sup>(10,11)</sup> led to the conclusion that the blue coloration of IPVA solutions is due to the presence of iodine ions with one positive valence, and that when the valence of iodine changes the blue coloration disappears, the maximum of which corresponds to  $\lambda \sim 620 \text{ m}\mu$ , and the antimicrobial action is also weakened; the disappearance of the other maximum at  $\lambda \sim 350 \text{ m}\mu$ , due to  $\text{JO}^-$  ions, leads to a complete loss of antimicrobial properties. According to data <sup>(1)</sup>, this occurs, in particular, during thermal treatment of solutions.

Our spectrophotometric studies of mixtures of 1% aqueous polyvinyl alcohol solution with solutions of  $\text{J}_2 + \text{KJ}$  showed that the process of formation of the blue complex is satisfactorily described by the equation  $K = \tau/(a + b\tau)$  (where  $K$  is the extinction coefficient for the band  $\lambda_{\text{max}} = 620 \text{ m}\mu$ ,  $\tau$  is the time elapsed from the moment of mixing the solutions, and  $a$  and  $b$  are constants)

and is practically completed after 6-7 days, with the maximum color intensity being attained at an equivalent ratio  $J_2/C_2H_3OH = 1/10$ .

An analogous equation describes the process of restoration of the color of solutions after their complete or partial decolorization, which occurs upon heating.

The dependence of the extinction coefficients of the band  $\lambda = 610 \text{ m}\mu$  on the ratio and magnitude of the initial concentrations of iodine and PVA was studied. In the composition-extinction coefficient diagram, a shift of the maximum was found with a decrease in the values of the initial concentrations of iodine and PVA. The nonconstancy of the equivalent ratio indicates the nonchemical nature of the "blue complex" iodine-polyvinyl alcohol.

Optical-density curves were constructed for a series of solutions with variable iodine concentration. The initial gentle rise of the curve in the region of low iodine concentrations (up to 0.04%) permits the assumption that in this case

the nature of the interaction of iodine with PVA differs from that at higher iodine concentrations.

It is of interest that the sorption-isotherm-type curves for the two PVA samples we studied do not differ substantially from one another, whereas the initial rate of “complex formation” for one of these samples is approximately twice as high as for the other. Apparently, it is precisely the initial rate that may serve as a measure of the difference between the samples.

Institute of High-Molecular Compounds  
Academy of Sciences of the USSR

Saratov State University  
named after N. G. Chernyshevsky

Received  
9 IX 1963

## CITED LITERATURE

1. S. N. Ushakov, DAN, **134**, 643 (1960).
2. S. N. Ushakov, DAN, **139**, 160 (1961).
3. S. N. Ushakov, E. M. Lavrent'eva, Inventor' s Certificate No. 138378.
4. S. N. Ushakov, Inventor' s Certificate No. 1405778.
5. S. N. Ushakov, Inventor' s Certificate No. 134868.
6. S. N. Ushakov, Inventor' s Certificate No. 1400575.
7. L. G. Bogomolova, S. N. Ushakov et al., *Problems of Blood Transfusion and Clinical Medicine*, 1962, p. 161.
8. J. D. Loconti, J. W. Cahill, *J. Polym. Sci.*, **49**, 2 (1961).
9. S. Veiler, P. A. Rebinder, DAN, **49**, 354 (1945).
10. S. N. Ushakov, V. O. Mokhnach, DAN, **128**, 1317 (1959).
11. V. O. Mokhnach, *Iodine Compounds with High Polymers, Their Antimicrobial and Therapeutic Properties*, Publishing House of the Academy of Sciences of the USSR, 1962, pp. 117, 165.

*Note: Figure translations are in progress. See original paper for figures.*

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*