

Study of Cryostructuration of Polymer Systems. XII. Poly(vinyl alcohol) Cryogels: Influence of Low-Molecular Electrolytes

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SYNOPSIS

The influence of the presence of low-molecular electrolytes in initial solutions of poly(vinyl alcohol) (PVA) on the results of cryotropic gelation of the polymer (gelation caused by the freezing-thawing) and on the swelling characteristics of PVA cryogels prepared in a salt-free medium were studied. The reinforcing ability of the electrolytes with respect to the gel strength for both alkaline element cations and simple low-molecular anions has been shown to be in agreement with the positions of these ions in corresponding lyotropic (Hofmeister) series. Namely, the ions (chaotropic ones), which are capable to interfere the H-bonding, disturbed somewhat the cryotropic gel-formation of PVA and facilitated the marked additional swelling of cryogels preliminary prepared in pure water medium, whereas the ions (antichaotropic ones), which are capable to promote the H-bonding, caused the formation of reinforced cryogels and resulted in the shrinking of cryogels prepared without salt additives. More pronounced effects were observed for anions as compared with cations. Some anomalous swelling behavior of PVA cryogel in Cs⁺-containing solutions was supposed to be associated with the formation of weak chelates. In addition to antichaotropic inorganic salts like NaF, rather high salting-out effects in respect to PVA were exhibited by well-soluble amino acid salts: glycine zwitter-ions, lysine monochlorohydrate, and monosodium aspartate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(vinyl alcohol) (PVA) cryogels—cryoPVAGs—are known to be prepared by the freezing-thawing of concentrated solutions of the polymer.¹⁻⁴ The resultant products of such a cryotropic gelation process are the heterogeneous thermoreversible gels, whose properties and structure depend on both PVA characteristics (polymerization degree, amount of residual acyl groups, polymer tacticity, and concentration) and conditions of freeze-treatment (temperature and duration of freezing, regimes of a thawing step, a number of freezing-thawing cycles, etc.).³⁻¹⁵ Naturally, the properties of the final materials (i.e., cryoPVAGs) and the efficiency of the gel-formation

itself are affected by the nature of low-molecular liquid used as a solvent in an initial system. For this purpose, either water,¹⁻¹⁶ dimethylsulfoxide,⁴ or their mixtures,¹⁷⁻²⁰ as well as some other mixed solvents of nonelectrolyte origin, for instance, water/polyol ones,^{21,22} were used.

CryoPVAGs, throughout recent years, were rather widely examined as promising gel materials for the application in medicine,²³⁻²⁷ biotechnology,²⁸⁻³⁰ the food industry,^{31,32} and so on. In these cases, along with PVA, various ionic substances can constitute into the compositions for the preparation of the cryogels, and also inorganic or organic ions can be components of liquid media, where cryoPVAGs should operate. Therefore, it is necessary to know how these species (low-molecular ions) will influence the formation of cryogels and their behavior in various aqueous solutions. Furthermore, as different ions possess dissimilar lyotropic properties, the studies

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of the influence of such ions on PVA cryogelation and on the gels already prepared in a salt-free medium would provide certain data on the interconnection between lyotropic (salting-out and salting-in) effects of the electrolytes used and the physicochemical features of the polymer system of interest. The goal of this work was to recognize the abovementioned peculiarities.

EXPERIMENTAL

Materials

PVA of the trademark 16/1 (NPO "Polivinilatsetat," Yerevan, Armenia) was utilized in the work. The technical-grade polymer was refined by reprecipitation from 7% aqueous solution into sevenfold volume excess of methanol. The polymer thus purified had a viscosity-average molecular weight of about 67 kDa and saponification degree of 98.5%.

All salts used were chemically pure grade (Reakhim, Russia); before use, they were dried in vacuo in the presence of anhydrous CaCl_2 and 3-Å molecular sieves.

Amino acids—glycine, lysine monochlorohydrate, and sodium aspartate—for the experiments were purchased from Reanal (Hungary); they were used without additional purification.

Electrolyte solutions were prepared on a bidistilled water.

Methods

PVA solutions for the production of cryogels were prepared either on a salt-free water or on the basis of particular electrolyte solution. Dry polymer powder was stirred in the solvent used, and after PVA swelling at room temperature for a night the polymer was dissolved by heating on a boiling water bath for 40 min. Hot viscous solutions obtained were filtered through the sintered glass filter to remove possible mechanical impurities.

CryoPVAGs for rheological tests were formed in duralumin cylindrical molds in accordance with the procedure described in detail elsewhere.^{7,10,33} PVA concentration in all cases was 14 g/dL, freezing temperature was -20°C , freezing duration was 24 h, and thawing rate was of around $0.2^\circ\text{C}/\text{min}$. The technique for the determination of an apparent instantaneous shear modulus for the cryoPVAGs thus prepared was reported in detail earlier.^{7,10,33}

Uniform spherical beads of PVA cryogel (diam. ~ 3 mm) was obtained from the 14% aqueous poly-

mer solution with the aid of special cryogranulating device³⁴ under the same (aboveindicated) freezing-thawing conditions. Swelling parameters of the beads in various electrolyte media were measured gravimetrically according to the method described by Tanaka and Irie³⁵ for Ca-alginate beads. For our purpose, five-bead portions of cryoPVAG, which were preliminary washed with water from a sol-fraction,¹⁰ were placed into 50-mL Erlenmeyer flasks, each containing 25 mL of the concrete solution. The samples were stored with periodical shaking for 48 h at room temperature ($22 \pm 2^\circ\text{C}$). Control tests have demonstrated that such a duration was sufficient to reach practically further unchanging swelling degrees. Then each bead was separated from an excess of a liquid with filter paper and weighed. The results obtained for every five-bead portion were averaged. Relative swelling index (S_{rel}) was calculated as the ratio of the weight of a bead swollen in an electrolyte solution (m_e) to the weight of the initial bead swollen in pure water (m_w):

$$S_{\text{rel}} = m_e : m_w$$

The differences between the densities of solutions used and water were omitted in the computations because these differences did not exceed 5% at the working concentrations of the salts (i.e., ≤ 1 mol/L).

PVA film was prepared by the casting of 5% aqueous solution of the polymer on a horizontal polyethylene surface followed by self-evaporation of the solvent for the film formation. Then the film was dried up to a constant weight over anhydrous CaCl_2 and 3-Å molecular sieves in vacuum desiccator. Swelling characteristics of PVA film in various liquid media were evaluated with the procedure of Voelkel.^{36,37} In this case, three pieces (~ 0.1 g each) of the film after their weighing were, each separately, immersed into 20-mL portions of the solution of interest, stored there with periodical stirring at room temperature for 6 days (preliminary tests showed the necessity of this time to reach the unchanging swelling degrees), and then were taken from the liquid. The excessive free moisture was removed from each swollen film piece with a soft cotton cloth; after that the film was weighed. As every initial piece of dry film had its own weight (m^i), the relative swelling index (S'_{rel}) was calculated from the formula

$$S'_{\text{rel}} = (m_e/m^i) : (m_w/m^i_w)$$

where m_e and m_w are the weights of the pieces swollen, respectively, in an electrolyte solution and water, whereas m_e^i and m_w^i are the initial dry weights of the corresponding pieces. The values S'_{rel} obtained for every solution examined were averaged.

RESULTS AND DISCUSSION

It is generally considered^{6,8,9,13,25,38-40} that the major type of intermolecular interactions, which are responsible for the stabilization of spatial network of cryoPVAGs, are multiple hydrogen bonds between OH-groups of the polymer chains in microcrystallinity zones; therefore, various ions possessing abilities to affect on these bonds will influence the PVA gel formation. Also, similar salt effects are well-known for numerous other water-compatible polymers, when both cations and anions of neutral low-molecular electrolytes in aqueous media can act on H-bonding of the partners: "water-water," "water-polymer," and "polymer-polymer."^{41,42} In respect to the influence of such ions on a stability (lifetime) of oscillating water clusters and on a conformation of water-dissolved macromolecules, the ions are usually categorized as lyotropic or Hofmeister series. Just according to the position of the ions in these series, we selected concrete salts of monovalent cations and anions for the studies of electrolyte influence on the formation of cryoPVAGs and on their properties.

Table I shows data on rheological characteristics of PVA cryogels produced in the presence of some salts. The results are expressed in terms of relative magnitudes, i.e., as the ratio of instantaneous shear modulus for a gel prepared with electrolyte additive

(G_e) to the same modulus of the gel formed when pure water was used as an initial solvent for PVA (G_w). This mode of data presentation permits to demonstrate very conveniently the trends of the ions' influence.

In the cation series (upper part of Table I), chaotropic ability of the species diminishes from Li^+ to Cs^+ , and it is seen that at any equal salt concentration, a gel strength is increased in the following order: Li^+ -containing system < Na^+ -containing < K^+ -containing < Cs^+ -containing one. Under variation of the electrolyte concentration, the final effect depended on the salt nature. If the fivefold rise in the content of Na^+ ions (from 0.05 to 0.5 mol/L) resulted in a moderate growth of the gel strength (by $\sim 36\%$), the same increase in the concentration of K^+ ions and, especially, Cs^+ ions led to the significant reinforcement (by 90–170%) of the salt-containing cryoPVAGs, whereas gels formed in the presence of Li^+ ions were turned out weaker. In the case of latter ions, their weakening influence began to manifest markedly at salt concentrations higher than about 0.3–0.4 mol/L, and strengthening ability of cesium ions was exhibited at much smaller concentration, namely, 0.05–0.1 mol/L.

Inasmuch as lithium chloride is the chaotropic agent, that is, the substance displacing opportunities to interfere the linking of H-bonds, and CsCl, in contrast, possesses the antichaotropic properties and can promote the H-bonding, the experimental data discussed have argued about the importance of hydrogen bonds for the formation of cryoPVAGs structure, its noncovalent network.

Regarding the "power" of the reinforcing influence on PVA cryogels, the cations of alkaline elements may be arranged as follows: Li^+ (weakens)

Table I Influence of Salts Added to the Initial PVA Water Solutions on Rheological Parameters of CryoPVAGs Formed

Influence of	Salt	G_e/G_w^a at Salt Concentrations (mol/L)					
		0.05	0.10	0.20	0.30	0.40	0.50
Cations	LiCl	1.03 ± 0.10	1.04 ± 0.10	0.99 ± 0.09	0.91 ± 0.07	0.79 ± 0.05	0.65 ± 0.04
	NaCl	1.10 ± 0.11	1.16 ± 0.12	1.24 ± 0.14	1.33 ± 0.14	1.34 ± 0.14	1.36 ± 0.15
	KCl	1.15 ± 0.10	1.20 ± 0.13	1.30 ± 0.11	1.47 ± 0.13	1.77 ± 0.15	1.88 ± 0.16
	CsCl	1.22 ± 0.13	1.37 ± 0.13	1.55 ± 0.16	1.84 ± 0.17	2.19 ± 0.21	2.69 ± 0.25
Anions	NaSCN	0.93 ± 0.06	0.87 ± 0.04	0.67 ± 0.04	0.56 ± 0.03	0.46 ± 0.02	0.37 ± 0.02
	NaBr	0.99 ± 0.08	0.92 ± 0.06	0.72 ± 0.05	0.61 ± 0.05	0.60 ± 0.04	0.58 ± 0.04
	NaCl	1.10 ± 0.11	1.16 ± 0.12	1.24 ± 0.14	1.33 ± 0.14	1.34 ± 0.14	1.36 ± 0.15
	NaOAc	1.11 ± 0.10	1.21 ± 0.14	1.36 ± 0.13	1.58 ± 0.15	1.87 ± 0.20	2.09 ± 0.19
	NaF	1.13 ± 0.09	1.27 ± 0.11	1.69 ± 0.15	2.63 ± 0.22	3.12 ± 0.26	3.41 ± 0.30

^a $G_w = 3.75$ kPa.

$< \text{Na}^+$ (low affects) $< \text{K}^+$ (reinforces) $< \text{Cs}^+$ (strongly reinforces). This sequence fully corresponds to the positions of the ions in cation lyotropic series.

The same studies on the influence of monovalent anions supplied experimental results, which are presented in the bottom part of the Table I. The sodium salts were used, because this cation in the concentration range 0–0.5 mol/L has exhibited, as it was pointed out above, a slight action on the PVA cryogelation. It is clearly seen that chaotropic anions (Br^- and, especially, SCN^-) significantly weakened cryoPVAGs, which were formed in the presence of corresponding salts, the effect being began to manifest at less electrolyte concentrations comparing to chaotropic cations. The latter fact reflects the known tenet⁴² that lyotropic properties of simple anions are higher than lyotropic properties of metal cations, mainly due to the greater solvation capacity of anions.

In turn, salts containing antichaotropic anions (OAc^- and, especially, F^-) facilitated the formation of very rigid PVA cryogels. For instance, cryoPVAG prepared in the presence of 0.5 mol/L of sodium acetate was twice stronger than the cryogel produced from salt-free water polymer solution, and the sample formed in the presence of 0.5 mol/L of sodium fluoride was turned out triple stronger. The reinforcing series for anions appeared to be as follows: SCN^- (significantly weakens) $< \text{Br}^-$ (weakens) $< \text{Cl}^-$ (low affects) $< \text{OAc}^-$ (reinforces) $< \text{F}^-$ (highly reinforces). And again, similar to cations, this sequence completely corresponded to the positions of such anions in the Hofmeister series.

All the data of Table I have evidently testified that during the formation of cryoPVAG, the chaotropic ions have hindered the interchain H-bonding and antichaotropic ones favored this type of interactions between PVA macromolecules. These observations did agree with long-described information on similar influence of the ions on PVA structuration in aqueous solutions at positive temperatures (see, for example, references 43 and 44). Therefore, as the latter conventional PVA gelation, as discussed here the cryotropic one, are controlled by identical forces, but the "extent" of their (i.e., forces) manifestation is dissimilar. This is reflected, for example, in the known differences of fusion temperatures of ordinary and freeze-induced PVA gels, when the former are melted at 25–35°C,^{45–47} and the latter ones at 60–80°C.^{3,5,6,9–11,22,33,38} The main reason is the concentrating effects^{7,48,49} taking place in the course of cryoprocessing, where the initial freezing-out of pure solvent (ice crystallization) increases

significantly the polymer content in unfrozen inclusions of the system in the so-called⁴⁸ liquid microphase. Due to this forced growth of the concentration of the gelling agent, the number of intermolecular contacts and the entanglement of chains are increased, thus resulting in more strong and more thermostable gel samples than those formed by the aging of PVA solutions at low positive temperatures without any freezing.

The data of Table I are concerned to the ion effects on the freeze-induced gelation of PVA solutions, but what about electrolyte influence on the cryoPVAGs already formed?

To investigate this problem, we prepared the cryogel in a beaded shape, washed out a sol-fraction (the yield of PVA cryogelation process in the conditions used is known to be 50–70%¹⁰), and then immersed the gel particles for swelling in solutions of chaotropic (LiCl , NaSCN) antichaotropic (CsCl , NaF), or low-influencing (NaCl) salts. As in this case, contrary to the presence of salts in initial PVA solution, there were no difficulties associated with the polymer precipitation by electrolyte solutions of high ionic strength, it was possible to increase the range of the salt concentration some higher 0.5 mol/L. Measuring the weight of the bead swollen in pure water and the weight of analogous bead swollen in particular solution, one could compute the relative swelling index – S_{rel} (see Experimental). Increase in this parameter higher than 1 (upswelling) would attest to the dissociation of some links in junction zones of cryoPVAG's spatial network, and a decrease in S_{rel} below 1 (deswelling) would be attributed to the compaction of the gel structure and arising of additional intermolecular links *de novo* during the soaking of the beads in corresponding salt solution. The results obtained are summarized in Table II.

It is seen that the increase in salt concentration from 0.05 to 1.0 mol/L for the cation series did not result in very large variation of osmotic characteristics of cryoPVAG. Thus, for the beads incubated in 1.0M LiCl solution, the upswelling effect did not exceed 6%; definite deswelling was inherent for the granules kept in NaCl solutions, but the influence of CsCl was rather specific (it was unclear why): initially slight increase in S_{rel} values and only then their diminishing with the salt concentration growth.

For the cations examined, the influence on the swelling behavior of cryoPVAG particles, which were immersed into salt solutions with electrolyte concentration of 1.0 mol/L, corresponds to the order Li^+ (slightly increases the swelling degree) $< \text{Cs}^+$ (moderately decreases the swelling degree) $< \text{Na}^+$

Table II Influence of Salts on the Relative Swelling Index of Beaded PVA Cryogel

Influence of	Salt	S_{rel} at Salt Concentration (mol/L)				
		0.05	0.10	0.25	0.50	1.00
Cations	LiCl	0.99 ± 0.05	1.01 ± 0.06	1.02 ± 0.06	1.03 ± 0.07	1.06 ± 0.04
	NaCl	1.00 ± 0.09	0.98 ± 0.07	0.95 ± 0.06	0.92 ± 0.05	0.79 ± 0.04
	CsCl	1.01 ± 0.06	1.04 ± 0.08	1.06 ± 0.05	1.02 ± 0.04	0.87 ± 0.03
Anions	NaSCN	1.02 ± 0.06	1.05 ± 0.06	1.10 ± 0.08	2.10 ± 0.13	3.95 ± 0.22
	NaCl	1.00 ± 0.09	0.98 ± 0.07	0.95 ± 0.06	0.92 ± 0.05	0.79 ± 0.04
	NaF	0.98 ± 0.04	0.94 ± 0.04	0.86 ± 0.03	0.74 ± 0.02	0.44 ± 0.02
	(NaF + NaSCN) ^a	1.00 ± 0.07	0.99 ± 0.06	0.98 ± 0.06	0.97 ± 0.05	0.90 ± 0.05

^a Equimolar mixture.

(some stronger affects than Cs^+). Contrary to the influence of the same ions on PVA cryogelation (Table I), Na^+ and Cs^+ ions changed their positions in such cation series.

The pattern for anions was more evident. The presence of chaotropic SCN^- ions in the systems under discussion caused (beginning from 0.2 to 0.3 mol/L of the salt concentration) a considerable additional swelling of cryoPVAG, whereas in the F^- -containing antichaotropic media, the marked decrease in S_{rel} was observed. It is of interest that in solutions of equimolar mixture of sodium rhodanide and sodium fluoride, the opposite lyotropic properties of the anions seem to be "overlap" each other, and some deswelling of PVA cryogel beads in 1.0M solution of the mixture could likely be attributed to the salting-out effect with increase in the ionic strength per se. For the anions tested, their order of the influence on S_{rel} values coincides with that in Hofmeister series: SCN^- (significantly increases the swelling degree of cryoPVAG) < Cl^- (moderately decreases the swelling degree) < F^- (considerably decreases the swelling degree).

Hence, the character of effects exerted by low-molecular electrolytes on the proper PVA cryogels had, as a rule, the "direction" similar to the influence of these salts on the cryotropic gel formation. The exception observed for Cs^+ cations has required the additional investigations for the elucidation the nature of the effect.

Taking into account that the swelling behavior of cryoPVAG beads is governed by the affinity of the solvent used to the polymer, that is, by the thermodynamic quality of the solvent, we tried to obtain such data in terms of Huggins' constants (k'), which are usually rather easy to calculate from the measurements of intrinsic viscosities. To our surprise, experimental values of k' in the case of PVA dissolved in solutions of antichaotropic salts (NaF,

NaOAc, CsCl) were extremely poor reproducible (apparently due to the uncontrolling association of PVA macromolecules) and, therefore, could not be used in consideration. To overcome these hindrances, the swelling parameters of dry PVA film were determined, inasmuch this approach (as it was demonstrated previously^{36,37,50}) gives unburied information on the interactions between the solvent and amorphous regions of the polymer (crystallites are rather poorly available in dry PVA for water molecules at room temperatures). The comparison of the swelling degrees of the film in salt solutions and its swelling in pure water evaluated the relative affinity of the electrolytes to the polymer.

At the concentrations of alkaline metal chlorides of 0.1–0.5 mol/L NaCl and KCl affected on S'_{rel} values very close, at $C_{salt} = 1.0$ mol/L, stronger salting-out ability was pronounced by the potassium chloride. In 0.1–0.25M solutions of LiCl, PVA film swelled practically to the same level as in the salt-free water; a weak diminishing (but not the growth) of S'_{rel} took place in the more concentrated systems, thus demonstrating certain differences in the influence of such LiCl solutions on PVA hydrogel (Table II), i.e., on the already solvated network and on the dry polymer (Table III). But in the LiCl concentration range studied, these differences were not so large. As for CsCl solutions, they were appeared to be "more chaotropic" than NaCl- and KCl-containing ones. This meant that, in general, a swelling behavior of both cryoPVAG and PVA film in 0.1–1.0M solutions of cesium chloride did not obey to the position of Cs^+ ions in the conventional lyotropic cation series. We were unable to find any suitable data on such an effect from the literature. In the article of Saito,⁴¹ published 25 years ago, there was the description of the influence of CsCl (0–0.5 mol/L concentrations) on the cloud temperatures of PVA solutions, but the polymer under study contained

Table III Relative Swelling Indexes of PVA Film in Aqueous Salt Solutions

Influence of	Salt	S'_{rel} at Salt Concentration (mol/L)			
		0.10	0.25	0.50	1.00
Cations	LiCl	1.05 ± 0.09	0.88 ± 0.07	0.83 ± 0.10	0.79 ± 0.07
	NaCl	0.83 ± 0.07	0.76 ± 0.07	0.69 ± 0.06	0.63 ± 0.05
	KCl	0.87 ± 0.08	0.77 ± 0.06	0.67 ± 0.06	0.57 ± 0.05
	CsCl	0.94 ± 0.08	0.79 ± 0.06	0.77 ± 0.07	0.66 ± 0.06
Anions	NaSCN	1.05 ± 0.09	1.21 ± 0.11	1.25 ± 0.14	1.56 ± 0.14
	NaBr	0.84 ± 0.07	0.83 ± 0.07	0.76 ± 0.06	0.74 ± 0.06
	NaCl	0.83 ± 0.07	0.76 ± 0.07	0.69 ± 0.06	0.63 ± 0.05
	NaOAc	0.83 ± 0.07	0.74 ± 0.05	0.68 ± 0.06	0.58 ± 0.05
	NaF	0.77 ± 0.06	0.66 ± 0.06	0.58 ± 0.05	(0.52 ± 0.05) ^a

^a At NaF concentrations of 0.75 mol/L.

30% of OAc-groups (i.e., degree of saponification was only 70% opposite to 98.5% in the PVA used in this work). No anomalies for the Saito system were observed.

We have no experimentally confirmed explanation for our results with this salt, although one potential reason could be noted. This is the suggestion about a weak coordination of outer vacant orbitals of cesium atoms with *n*-electron pairs of OH-groups in PVA. Such hypothetical interactions could, in principle, increase the affinity of the salt to the polymer and decrease the salting-out ability of CsCl in respect to this particular macromolecules. The exhibition of the effect at positive temperatures (Tables II and III) but not in the frozen systems (Table I) can be the consequence of the considerable rise in the CsCl content in liquid unfrozen microphase, where, at these increased concentrations of the salt, its salting-out action is apparently becoming dominant.

Anion series for the case under discussion (bottom part of Table III) was, similar to the swelling of cryoPVAG beads in the same solutions (Table III), in good agreement with the position of the anions in the lyotropic sequence. In other words, no additional specific interactions (like to PVA/Cs⁺ ones) were, obviously, inherent for the influence of these anions on the solvation of PVA film by the electrolyte solutions examined (for NaF, because of the solubility limit, the highest available concentration was 0.75 mol/L). Hence, one can conclude that salt effects taking place under immersion of the wet beads of PVA cryogel, as well as of dry PVA film, into the above liquid media were, generally, the same in their physicochemical origin.

The last question concerning the influence of low-molecular electrolytes on PVA cryogels, which we

were interested in this work, was the problem of salt effects induced by charged organic substances. For the experiments, three typical well-soluble amino acids were selected. First, glycine has one amino and one carboxyl groups in a molecule; in aqueous solutions at neutral pH, this amino acid exists as a zwitter-ion. The second representative, lysine, is related to the basic amino acids and bears one carboxyl and two amino groups; this one was used as monochlorohydrate to prevent a shift of pH toward alkaline region. The third organic electrolyte, aspartic acid, contains one amino and two carboxyl groups; this specimen was used in the form of monosodium salt to inhibit pH shift to acidic zone. The data on the influence of given amino acids on the results of PVA cryogelation, swelling characteristics of cryoPVAG beads, and swelling behavior of PVA film are accumulated in Table IV.

It is seen that all these charged organic compounds can be assigned to the agents favoring the formation of cryogels, as the latter ones have been gained more rigid (G_e/G_w values ≥ 1 , Table IV) than those prepared in the pure water medium. The antichotropic tendencies were also observed in respect to the influence of these substances on S_{rel} and S'_{rel} magnitudes. The results obtained have demonstrated rather high salting-out ability of similar well-water-soluble amino acids (other ones, for instance, aromatic amino acids—phenylalanine, tyrosine, or tryptophan—possess low water solubility). Such structurizing ability is, apparently, due to the strong hydration of glycine, lysine⁻HCl, and sodium aspartate and their competition with PVA macromolecules for a water.

Among the data of Table IV, a very pronounced effect of the presence of 0.5M sodium aspartate in the initial polymer solution on the relative strength

Table IV Influence of Well-Soluble Amino Acids on the Properties of PVA Cryogels and Swelling Index of PVA Film

Organic Electrolyte	Concentration (mol/L)	Parameter Determined		
		G_e/G_w	S_{rel}	S'_{rel}
Glycine	0.05	1.09 ± 0.10	—	—
	0.10	1.23 ± 0.11	0.99 ± 0.05	0.82 ± 0.08
	0.25	1.40 ± 0.13	0.97 ± 0.04	0.80 ± 0.07
	0.50	2.29 ± 0.18	0.86 ± 0.04	0.74 ± 0.06
	1.00	—	0.74 ± 0.02	0.61 ± 0.05
Lysine monochlorohydrate	0.05	0.95 ± 0.09	—	—
	0.10	0.97 ± 0.10	0.98 ± 0.08	1.08 ± 0.09
	0.25	1.07 ± 0.10	0.96 ± 0.06	0.87 ± 0.08
	0.50	2.20 ± 0.16	0.84 ± 0.05	0.70 ± 0.05
	1.00	—	0.62 ± 0.02	0.57 ± 0.04
Monosodium aspartate	0.05	1.17 ± 0.12	—	—
	0.10	1.36 ± 0.12	0.92 ± 0.09	0.95 ± 0.08
	0.25	2.93 ± 0.22	0.85 ± 0.07	0.80 ± 0.07
	0.50	10.7 ± 0.3	0.59 ± 0.03	0.67 ± 0.06
	1.00	—	0.30 ± 0.02	0.51 ± 0.04

of cryoPVAG and also a considerable shrinking action of aspartate solutions on the cryogel beads engaged our attention. These effects attested on very powerful antichaotropic properties of concentrated (≥ 0.5 mol/L) aspartate solutions, i.e., on the extremely high potential of the substance to facilitate the H-bonding in the PVA-containing systems. It seems likely that the this amino acid salt should exhibit the same kind of influence on other water-compatible macromolecules as well.

CONCLUSION

In the Introduction, we pointed out that PVA cryogels attract significant attention in several applied fields, especially for some biomedical purposes. Clearly, during usage of similar gel materials in a contact with various biological liquids (blood, lymph, cultural media, etc.), numerous charged (mainly salts) and noncharged substances have an effect on cryoPVAG. The data showing basic trends of such an influence of low-molecular electrolytes were obtained in this work. These experimental results obviously testify about the coincidence in the character of the influence of both cations and anions with their positions in corresponding cation or anion lyotropic series. Some minor exceptions could, perhaps, be attributed to the possible specific interactions (for instance, chelating) between PVA hydroxyl groups and coordination sphere of a complexing ion.

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