

Poly(acrylic acid)—poly(vinyl pyrrolidone) complexes in solutions*

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Received 24 July 1975

Accepted for publication 14 April 1976

By means of conductometric and potentiometric methods it has been shown that the composition of poly(acrylic acid)—poly(vinyl pyrrolidone) complexes is equimolar. The limiting viscosity numbers $[\eta]$ of polycomplexes in water are about $10 \text{ cm}^3/\text{g}$ and sedimentation constants S_0 are about 25 s. It indicates a rather compact structure of the complex particles. Both the sedimentation constants and the limiting viscosity numbers in aqueous solutions do not depend on the molecular weight of the matrix.

A sharp increase of viscosity and decrease of sedimentation constants is observed when using dimethyl sulfoxide as a solvent. The cooperative character of the changes in $[\eta]$ and in S_0 allows us to assume that the polymer complex is destroyed in the organic solvent.

The observed difference in properties of polyacid (polymethacrylic, polyacrylic)—poly(vinyl pyrrolidone) complexes is due to the chemical nature of the macromolecular matrix.

Кондуктометрически и потенциметрически было доказано, что состав комплексов полиакриловой кислоты и поливинилпирролидона является эквимольным. Характеристическая вязкость комплексов в воде $[\eta]$ равна $\sim 10 \text{ см}^3/\text{г}$ и константы седиментации S_0 равны ~ 25 сек. Это показывает, что частицы комплексов имеют сравнительно компактную структуру. Ни константы седиментации ни характеристические вязкости в воде не зависят от молекулярного веса матрицы.

При переходе к диметилсульфоксиду наблюдается резкое возрастание характеристической вязкости и уменьшение константы седиментации. Кооперативный характер величин $[\eta]$ и S_0 позволяет предполагать разложение полимерных комплексов.

Наблюдаемая разница в свойствах комплексов поликислот (полиметакриловой и полиакриловой) с поливинилпирролидоном вызвана разницей в химической природе высокомолекулярной матрицы.

Recently, the attention was paid to the investigation of interactions between polymer components. These reactions are of great interest from the point of view of polymer modification because the resulting complexes possess some unique properties essentially different from those of the original polymers. Moreover,

* Presented at the 4th IUPAC International Conference "Modified Polymers, Their Preparation and Properties", Bratislava, July 1—4, 1975.

reactions between macromolecular components make it possible to model processes in biological systems.

We have already investigated the properties of poly(methacrylic acid)—poly(vinyl pyrrolidone) (PMAA—PVP) complexes in solutions [1, 2]. It has been found that complexes with specific hydrodynamic properties are formed in water. It was of interest to observe the influence of the chemical nature of the matrix (a high molecular component) on properties of complexes. With this purpose poly(acrylic acid)—poly(vinyl pyrrolidone) (PAA—PVP) system has been investigated with PAA of various molecular weight.

Experimental

Poly(acrylic acid) was obtained by polymerization in dioxan solution at 70°C with benzoyl peroxide as initiator (0.06% of monomer weight). The polymer was fractionated by precipitation from dioxan solutions by petroleum ether. The intrinsic viscosity of fractions was measured with an Ubbelohde viscometer. The corresponding molecular weights were calculated by means of the equation $[\eta] = 10.09 \times 10^{-4} \times M^{0.74}$ (methanol, 30°C) [3] (Table 1).

Table 1

Molecular characteristics of complexes of PAA fractions with PVP

Fraction	PAA		PAA—PVP				
	<i>a</i>		<i>b</i>			<i>c</i>	<i>d</i>
	$[\eta]$	$M_v \cdot 10^{-3}$	$[\eta]$	$S_0 \cdot 10^{13}$	$\bar{M}_m \cdot 10^{-3}$	$[\eta]$	$[\eta]$
1-II	2.4	813	0.11	25.8	1623	1.36	0.08
1-I	1.88	597	0.12	25.9	1699	1.32	0.08
3-I	1.40	400	0.10	24.6	1436	0.96	0.09
5-II	1.18	318	0.07	21.4	980	0.72	0.10
3-III	1.00	254	0.07	24.0	1162	0.91	0.07
5-I	0.88	214	0.10	26.2	1582	0.56	0.09
6-II	0.62	133	0.07	20.7	928	0.44	0.08
5-III	0.44	83	0.08	22.1	1097	0.41	0.08

a) Methanol, 30°C; *b)* H₂O, 25°C, $(1 - \bar{v}\rho) = 0.223$, where \bar{v} is the partial specific volume of the polymer and ρ is the solvent density; *c)* DMSO, 25°C; *d)* DMSO : H₂O = 1 : 1.

Poly(vinyl pyrrolidone) was a commercial product of BDH Co. (England) with viscometric molecular weight $M_v = 50 \times 10^3$ [4].

Sedimentation constants S_0 were measured by means of an analytical ultracentrifuge MOM-120 (Hungary) at 25°C and 30 000 rpm in water with the Philpot—Svensson optical system and phase-contrast plate. Hydrodynamic average molecular weights \bar{M}_m of complexes were calculated from viscosity and sedimentation data by means of the Flory—Mandelkern invariant β' [5]; the value $\beta' = 2.16 \times 10^6$ was used (*cf.* Ref. [1]).

Conductometric measurements were carried out using a conductometer OK-102 (Hungary).

Polymer complexes were prepared by mixing the initial polymer solutions.

Results and discussion

The investigation of stoichiometry of poly(acrylic acid)—poly(vinyl pyrrolidone) complexes [6, 7] indicates an equimolar composition of the complexes. Our results of conductometric titration of 0.01 N polyacid aqueous solutions with 0.1 N-PVP solutions are in a good agreement with literature data (Fig. 1): the minimum on the curve corresponds to 1:1 ratio of polymer components. When acetic acid was used, no extreme value of electrical conductivity was determined. Evidently some critical length of the interacting macromolecules is required for the polymer complex formation [8, 9].

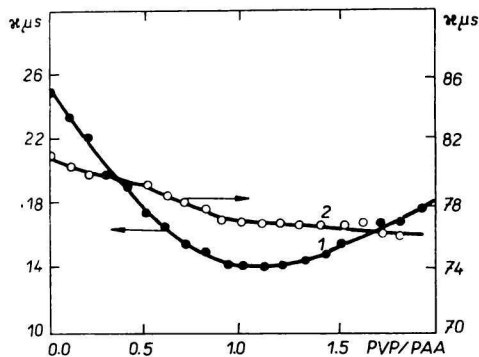


Fig. 1. Curves of conductometric titration of aqueous solutions of poly(acrylic acid) (1) and acetic acid (2) with poly(vinyl pyrrolidone). κ denotes specific conductivity (μS) [4].

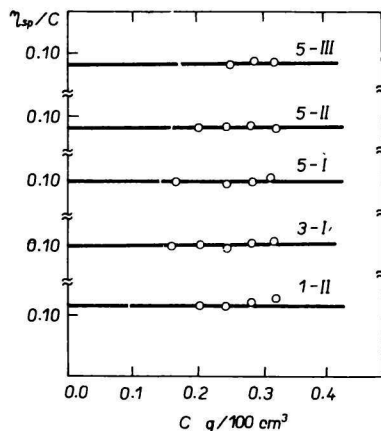


Fig. 2. Concentration dependence of reduced viscosity of aqueous solutions of complexes formed by PVP and fractions of PAA. Figures at lines denote the fractions of PAA (cf. Table 1).

The intrinsic viscosities and sedimentation constants of PAA—PVP complexes in water were measured with PAA of various molecular weight (Table 1, Fig. 2).

From the analysis of the obtained data it is evident that:

1. the limiting viscosity number of complexes is very low (about $10 \text{ cm}^3/\text{g}$) and close to the limiting viscosity number of globular proteins. The sedimentation constants have high values ($S_0 \sim 23 \pm 3 \text{ s}$).

2. The concentration dependence of the reduced viscosity of aqueous solutions was negligible.

3. The limiting viscosity numbers and sedimentation constants of aqueous solutions of complexes do not depend on the molecular weight of the matrix (Table 1).

As it is seen from Table 1 the hydrodynamic average molecular weight \bar{M}_{m} of complex particles does not change with the length of the PAA chain. It allows to

suggest in accordance with [1, 2] an intermolecular association of complex particles in water, the degree of which is determined by the matrix molecular weight.

The properties of PAA—PVP system were examined in mixed solvents water—dimethyl sulfoxide (DMSO). It is evident from Fig. 3 and Table 1 that in mixtures containing DMSO up to 50 volume % the complex probably remains stable, this being confirmed by the low values of $[\eta]$. However, with further increase of DMSO content a sharp increase of viscosity and decrease of sedimentation constant are observed in a narrow interval of the solvent composition. The cooperative character of the $[\eta]$ and S_0 changes allows us to suppose that in DMSO and in mixtures with high content of DMSO not only a weakening of lyophobic interactions takes place but also the destruction of hydrogen bonds and hence of the polymer complex itself. The dependence of the limiting viscosity number (Table 1) on the molecular weight of polymers appears in DMSO.

The temperature dependence of viscosity of the complex has been studied in the interval 25—100°C. In water the limiting viscosity number does not depend on the temperature (Fig. 4), *i.e.* the complex is stable and it is not destroyed by heating.

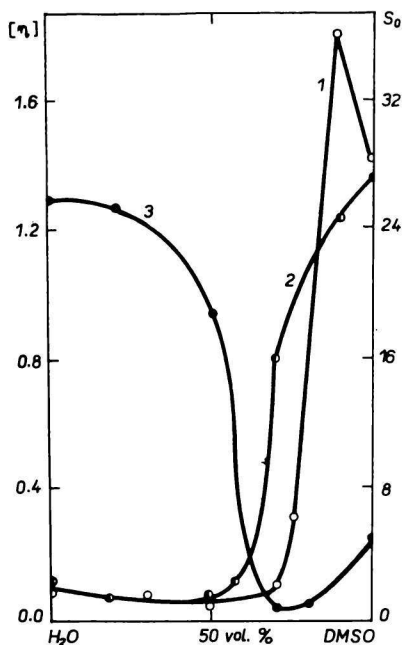


Fig. 3. Dependences of limiting viscosity numbers of complexes PMAA—PVP (1) and PAA—PVP (2) and sedimentation constants of PAA—PVP complexes (3) on composition of mixed solvent H₂O—DMSO.

M_n of PMAA = M_n of PAA = 8×10^5 .

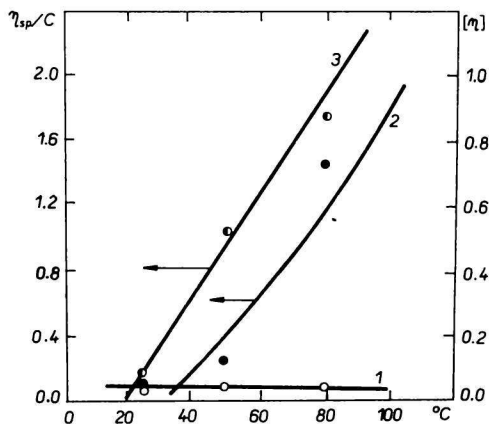


Fig. 4. Temperature dependence of limiting viscosity numbers of PAA—PVP complexes in water (1) and of reduced viscosity in mixtures H₂O—DMSO (50 : 50 volume %, curve 2) and (40 : 60 volume %, curve 3).

That may be related apparently to the increase of hydrophobic interactions which are predominant in the stabilization of compact structure of the complexes in water [10]. A different situation is observed in mixtures containing 50 and 60 volume % of DMSO. In these mixtures the complex remains intact ($[\eta] = 8$ and $12 \text{ cm}^3/\text{g}$, respectively) at 25°C , but if the temperature increases the complex dissociates. This is indicated by a strong increase of reduced viscosity and by its anomalous concentration dependence. In water—organic solvent systems the principal role in complex formation belongs probably to H bonds, which are weakening on heating.

It is interesting to compare the behaviour of poly(methacrylic acid)—poly(vinyl pyrrolidone) [1, 2] and poly(acrylic acid)—poly(vinyl pyrrolidone) complexes in solutions. It is known that the hydrodynamic properties of particular polyacids in aqueous solutions are very different. This can be explained [11, 12] by the presence of the secondary structures in PMAA molecules stabilized mainly by hydrophobic interactions of methyl groups in aqueous media. It can be expected that the structure formation of PMAA involves higher stability of its complexes with PVP. Indeed, due to a higher hydrophobization, PMAA—PVP complexes are very poorly soluble in water (the maximum concentration is about $0.1 \text{ g}/100 \text{ cm}^3$) whereas PAA—PVP complexes remain in solutions at concentrations about 0.3 — $0.4 \text{ g}/100 \text{ cm}^3$ (Fig. 2). In mixed water—DMSO solvents the complexes in the PMAA—PVP system preserve their compact structure at a higher content of DMSO (about 70 volume %, Fig. 3) as compared with the PAA—PVP system. A sharp increase of limiting viscosity number at further increase of DMSO content is observed for the PMAA—PVP complexes in a narrower interval of the solvent composition and has a more pronounced character.

Thus the difference in behaviour of PMAA—PVP and PAA—PVP complexes is ascribed to the presence of secondary structures of molecules of PMAA, *i.e.* to the difference in the chemical nature of the polymer matrix.

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