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CHAINLENGTH EFFECTS ON INTERACTIONS OF POLYVINYLPYRROLIDONE WITH LOW AND HIGH MOLECULAR COMPOUNDS

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Abstract—Very narrow fractions of polyvinylpyrrolidone (PVP) for a range of low molecular weight from $20 \cdot 10^3$ to $\sim 10^3$ were prepared by gel filtration using sephadex gel. Interactions between fractions of different M_n and small molecules (iodine and 1-anilinonaphthaline-8-sulphonate) and polymers (polymethacrylic and polyacrylic acids) were studied in aqueous solution. The ability of PVP to form complexes with low molecular weight compounds depends on chainlength. The greatest loss of the ability was observed for PVP with M_n on passing from $5 \cdot 10^3$ to $\sim 10^3$. The chainlength effects for PVP are accounted for an unlike dehydration and unlike "local" link concentration near links for these macromolecules in water. For PAA and PMAA, the threshold values of $\bar{M}_n$, below which there is the beginning of weakening of complexation for PVP, are $6 \cdot 10^3$ and $2.5 \cdot 10^3$ respectively. The difference of the complex formation for these polyacids appears to be related to hydrophobic interactions between the α-methyl groups of PMAA and nonpolar regions of PVP.

The elucidation of mechanisms of interaction for synthetic macromolecules with low and high molecular compounds requires study of the effects of chainlength on complex formation. The results are useful for understanding of catalytic "polymer effects" [1–3] and polymer-polymer complexation [4–6]. Important information about polymer sorption might be obtained by study of the complexation of polyvinylpyrrolidone (PVP) of various molecular weights in aqueous solutions with both small molecules and macromolecules. This water-soluble polymer is known to interact with phenols [7,8], detergents [9], dyes [10] and polyacids [11,12]. In many studies of PVP properties, however, the work involved unfractionated samples. Data on the chainlength effect for PVP at low polymerization degrees on the complexation between this polymer and some of above mentioned compounds in aqueous solution are not available.

In the present work the formation of complexes for PVP fractions with (i) iodine in aqueous solution of potassium iodide and the fluorescent probe, 1,8-anilinonaphthalene-8-sulphonate (ANS), (ii) polyacrylic (PAA) and polymethacrylic (PMAA) acids was studied. The preparation of the PVP fractions of the narrowest molecular weight distribution was performed by gel filtration using sephadex gel.

EXPERIMENTAL

PVP samples with $\bar{M}_w > 20 \cdot 10^3$ were obtained by radical polymerization of *N*-vinylpyrrolidone (VP) (t_b 86 at 8 mm, $n_D^{20} = 1.5132$) in aqueous solution with azobisisobutyronitrile as initiator. The samples of PMAA with $\bar{M}_w = 500 \cdot 10^3$ and PAA with $\bar{M}_w = 300 \cdot 10^3$ were synthesized by radical polymerization of the acids.

PVP polymers with low molecular weight, i.e. $\bar{M}_w = 20 \cdot 10^3$ and $10 \cdot 10^3$, were prepared by polymerization in the presence of H_2O_2 and NH_3 [13]. These polymers were repeatedly precipitated from ethanol solution with diethylether to remove traces of monomer and 2-pyrrolidone; removal of these substances was checked by u.v.-spectroscopy and gas–liquid chromatography.

Preparative fractionation of PVP with $\bar{M}_w = 20 \cdot 10^3$ and $10 \cdot 10^3$ was carried out using sephadex gels. G-100 and G-75 (1:1) in 3 × 50 cm column were used. Twenty fractions were obtained from one gram. The molecular weights of these fractions were calculated from viscosities by the equation $[\eta] = 1.9 \cdot 10^{-4} \bar{M}_w^{0.68}$ in water at 25 ± 0.1 [14]. The molecular weights of unfractionated polymers were estimated by the viscosity technique using the equation $[\eta] = 1.3 \cdot 10^{-4} M^{0.68}$ in water [14]. Elution curves of the PVP fraction were obtained using 1.5 × 30 cm column involving G-200, G-100 and G-75 (1:1:1) and 1 × 50 cm column involving G-75 and G-50 (1:1). A PVP fraction separation efficiancy for the gel was evaluated with polyethylenglucol (PO) with $\bar{M}_w \simeq \bar{M}_n = 15 \cdot 10^3$, $6 \cdot 10^3$, $4 \cdot 10^3$, $2 \cdot 10^3$, 10^3, 600 and 400 (Fluka) as a standard. The PVP and PO concentration in water were controlled by absorption at $\lambda = 225$ and 200 nm, respectively.

Methods

Spectrophotometric measurements of the complexes for PVP with iodine and fluorescence measurements of the probe in the presence of PVP were carried out with a "Perkin-Elmer-402" spectrophotometer and "Aminco" spectrofluorometer, respectively. The viscosities were measured in an Ubbelohde viscometer at 25 ∓ 0.1 .

RESULTS AND DISCUSSION

Polyvinylpyrrolidone and small molecule interaction

Figure 1 shows the visible spectra of absorption for iodine aqueous solutions involving KI in the absence and the presence of the polymer and that for the same solution containing a low molecular weight analogue, 2-methylpyrrolidone; there is no absorption of the pyrrolidone compounds over the range of the spectra studied. As seen in Fig. 1, the addition of PVP results in an increase of optical density of the iodine solution between 270 and 600 nm.

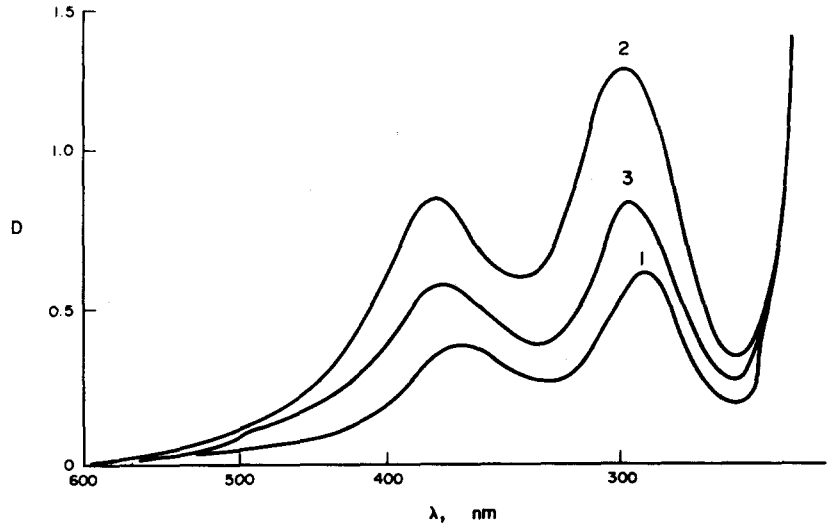

Fig. 1. Visible spectra of aqueous solutions for I_2 and KI in the absence (1) and the presence of polyvinylpyrrolidone with $\bar{M}_w = 1.5 \cdot 10^6$, $3.5 \cdot 10^5$ and $2.5 \cdot 10^4$(2), $3 \cdot 10^3$ (3). Experimental conditions $[I_2] = 10^{-4}$ M, $[KI] = 5 \cdot 10^{-4}$ M, $[PVP] = 1.8 \cdot 10^{-2}$ M, 25°.

The 2-methylpyrrolidone has no effect on the iodine spectra of the iodine solution. The absorbance increase and the shift of absorption maximum for the solution being examined in the presence of PVP demonstrate complex formation between PVP and I_3^- ions [15]. It was found that the complex absorption remains practically unchanged on introducing PVP with $\bar{M}_w = 1.5 \cdot 10^6$, $3.5 \cdot 10^5$ and $2.5 \cdot 10^4$ to the solution at PVP concentrations exceeding considerably the I_3^- concentration and decreases on introducing PVP with $\bar{M}_n = 3 \cdot 10^3$ (Fig. 1). The data and lack of change for the complex absorption of the I_3^- solution in the presence of 2-methylpyrrolidone indicates that the ability of the macromolecules to bind I_3^- ions depends on the molecule weight of the macromolecule being in the range from $2.5 \cdot 10^4$ to 100 (molecular weight of the analogue.

Addition of PVP to fluorescent probe solution increased the fluoresence intensity (Fig. 2). The use of unfractionated PVP samples with $\bar{M}_w = 1.5 \cdot 10^6$, 10^5, $2.5 \cdot 10^4$, 10^4 causes no change of fluorescence intensity for PVP-ANS complexes. The analogue, at concentrations from 10^{-4} to 10^{-1}M, has no effect on the intensity of the probe (Fig. 2). The data indicate that the interaction of the macromolecule and these compounds change over a range of PVP molecular weights, from 10^4 to 10^2.

It is worthwhile to note an increase of the fluorescence intensity of the probe in PVP complexes. It is known that the probe molecules bound to the hydrophobic regions for certain biological macromolecules possess an increased fluorescence intensity [16] compared to that of the probe in water. In the present case, considerable enhancement of the fluorescence intensity for an ANS molecule surrounded by PVP chainlinks against that of the ANS molecule surrounded by water molecules (150 times [17]) indicates the presence of hydrophobic interaction between regions of the PVP chains. It is of interest that, unlike the PVP macromolecules, water-soluble polymers such as PO, polyvinylalchohol, dextran do not affect the fluorescence of the probe [17].

Since the interaction of the PVP molecules with the reagents was found to depend on the molecular weight over a range of low molecular weights, study

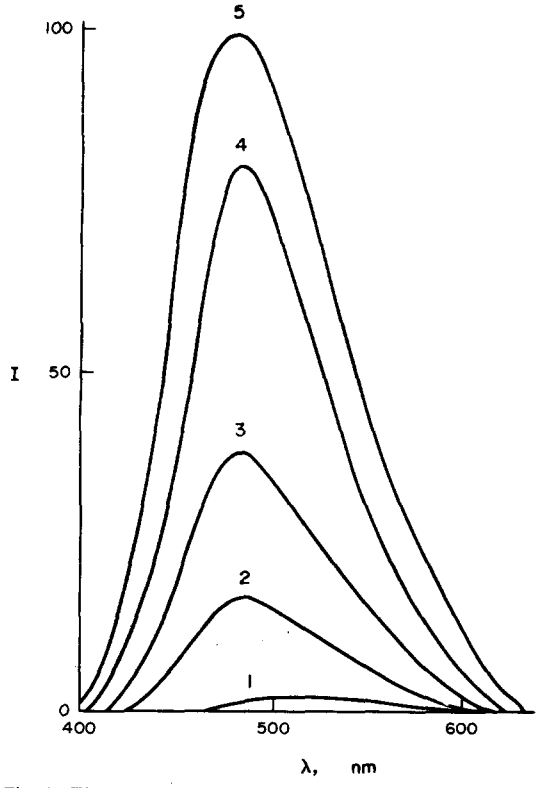

Fig. 2. Fluorescence spectra of 1.8-ANS aqueous solutions in the presence of different concentrations for PVP: 0 (1); $1.25 \cdot 10^{-3}$ (2); $2.5 \cdot 10^{-3}$ (3); $5 \cdot 10^{-2}$ (4); $5 \cdot 10^{-1}$ M (5). Experimental conditions: $[ANS] = 10^{-5}$ M, pH 6.0, λ of exciting light 365 nm, 25°.

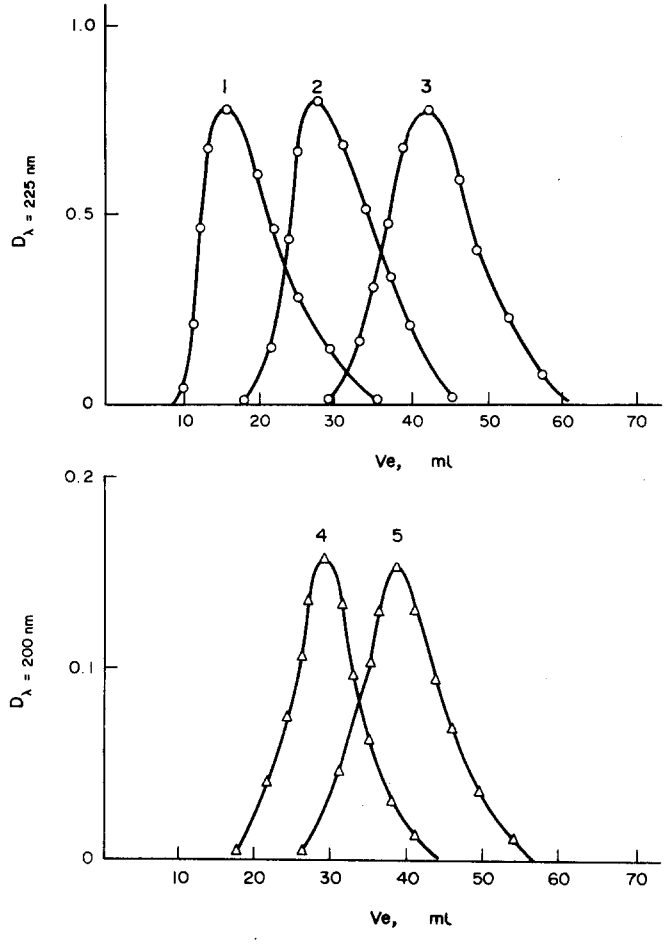

Fig. 3. Elution curves for PVP fractions with $\bar{M}_n = 40 \cdot 10^3$ (1), $8 \cdot 10^3$ (2) and $3 \cdot 10^3$ (3) and polyethyleneglycoles with $\bar{M}_w \simeq \bar{M}_n = 6 \cdot 10^3$ (4) and $2 \cdot 10^2$ (5). Experimental conditions: 25°, water and G-75:G-100:G-200 (1:1:1).

was made of sorption properties of PVP fractions with $\bar{M}_n$ from 10^3 to 10^4. The elution curves of the fractions obtained from the PVP sample with $\bar{M}_w = 20 \cdot 10^3$ are presented in Fig. 3. Certain positions of the elution curve maximum are characteristic of the PVP fraction with different $\bar{M}_n$ ($\bar{M}_w \simeq \bar{M}_n = 40 \cdot 10^3$ to $2 \cdot 10^3$). This fact confirms high resolution capability of the gel relative to macromolecules with unlike chainlengths. Comparison of the elution curves for PVP fractions and the polyethyleneglycol samples ($\bar{M}_w = 15 \cdot 10^3$ and $6 \cdot 10^2$) indicates about a narrow enough molecular weight distribution for the PVP fractions to be made. There is linear dependence of log $\bar{M}_n$ on elution volumes (V_e) for molecular weights from $40 \cdot 10^3$ to $2 \cdot 10^3$ (Fig. 4).

However, these fractionated PVP samples, as seen in Fig. 3, contain some macromolecules with unlike molecular weights. Correct estimation of the chainlength at which the change of complex formation occurs requires the use of a monodisperse sample. Therefore preparation of a PVP fraction approaching monodisperse was carried out. The high sensitivity of spectral methods used in the investigation permits study of complex formation for PVP at very low concentration in solution (10^{-4}–10^{-3}M).

One of the PVP fraction (100 mg) obtained preparatively was separated into 10–15 fractions (Fig. 4). After a certain volume of each fraction had been

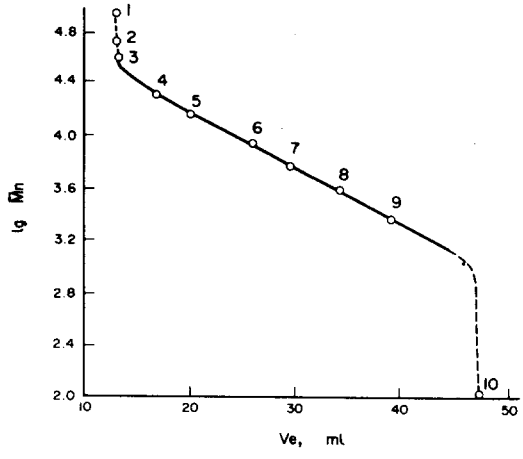

Fig. 4. Dependence of log $\bar{M}_n$ for PVP on elution volume (V_e). $\bar{M}_n$: $30 \cdot 10^4$ (1); $12 \cdot 10^4$ (2); $4 \cdot 10^4$(3); $2 \cdot 10^4$ (4); $1.4 \cdot 10^4$ (5); $0.9 \cdot 10^4$ (6); $0.6 \cdot 10^4$ (7); $0.4 \cdot 10^4$ (8); $0.3 \cdot 10^4$ (9) and 2-methylpyrrolidone (10).

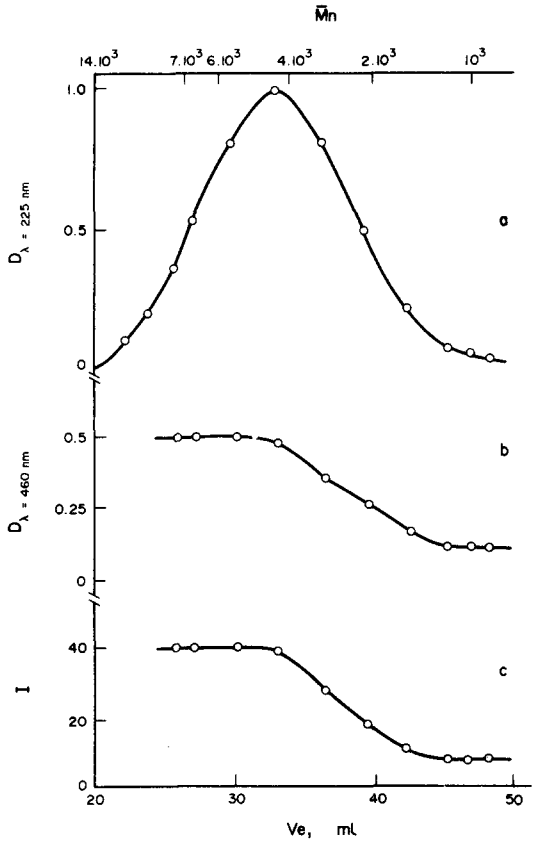

Fig. 5. Elution curve of PVP fraction with M_n $4 \cdot 10^3$ (a), dependence of absorbance ($D_{\lambda\ 460\,nm}$) of KI_3 (b) and fluorescence intensivity ($I_{\lambda\ 480\,nm}$) of 1-anilinonaphthaline-8-sulphonate Mg (c) on V_e or M_n at constant concentration for PVP. Experimental conditions: [ANS] = 10^{-5}M, [I_2] = $5 \cdot 10^{-4}$M, [PVP] = $2.5 \cdot 10^{-3}$M in every fraction, 25°.

added to the iodine aqueous solution, the optical density of this solution was measured. Using the dependence of log $\bar{M}_n$ on V_e, one can estimate a molecular weight range for which there is a change of optical density characterizing the complex concentration in the solution with constant [PVP] and [I_3^-] (Fig. 5). Figure 5 shows that the value of $D_\lambda = 460$ nm for the solution containing PVP molecules with $\bar{M}_n$ from $10 \cdot 10^3$ to $5 \cdot 10^3$ is independent of the molecular weight and it exceeds $D_{\lambda=460\,nm}$ for the solution without PVP. The former decreases with decreasing PVP molecular weight and approaches the same $D_{\lambda=460\,nm}$ value as that of the initial solution for PVP macromolecules with $\bar{M}_n = 1.5$ to $1.0 \cdot 10^3$. Thus the PVP macromolecules in the range of $\bar{M}_n$ from $1.5 \cdot 10^3$ to $5 \cdot 10^3$ possess unlike affinity to I_3^- ions.

A similar effect was found on studying the interaction of the probe and PVP. As seen in Fig. 5, a fall of the fluorescence intensity (I_k) occurs for practically the same range of $\bar{M}_n$ ($5 \cdot 10^3$ to $\sim 10^3$) as for the PVP—I_3^- system. The values I_k for the solutions containing PVP with $\bar{M}_n > 5 \cdot 10^3$ remain constant and for the solution containing PVP with $\bar{M}_n > 10^3$ approach that of the probe solution without PVP.

It should be noted that the PVP solutions without the probe do not show fluorescence intensity and have no effect on the independence of I_k upon V_e (or $\bar{M}_n$). Consequently the data confirm that the ability of PVP to interact with the small molecules studied depends on $\bar{M}_n$: a sharp enhancement of the ability occurs for macromolecules with polymerization degree from 10–15 to 50.

It has been reported [18] that the minimum number of chainlinks in a PVP macromolecule with molecular weight ($\bar{M}_w = 10^6$) entering in a complex involving aromatic molecules is 10 ∓ 3. Recently, it was shown [19] that the minimum number of chainlinks in polyvinylacetate (PVA) macromolecules when interacting a I_3^- ion in an ethanol-water mixture is 10–12. The data obtained in the present study are consistent with the reported results [19].

One can indicate two factors connected with the transition in the ability for complex formation of the macromolecules over the stated range of $\bar{P}$. The first factor is that enhancement of collisions between a small molecule and links of a chain with increasing $\bar{P}$ results from a growth of a local link concentration in the macromolecule in going from 10 to 50 links. The increase of the effective local concentration in going from an oligomer to a polymer was shown theoretically by Monte-Carlo calculation for flexible chains in a good solvent [20].

This local concentration ($\rho_{loc.}$) of links near a chain rather than that of links within a coil volume is likely to be of great importance for the interaction of the small molecule and the polymer molecule [21]. The local concentration for flexible chain macromolecules (e.g. partially quaternized poly-4-vinylpyridine) was found to be about 0.4M by the spin-label procedure [22], independent of polymerization degree from 70 to 2800 [21]. It is interesting that the interaction of PVP with the compounds studied in the same range of $\bar{P}$ remains constant.

The second factor is likely to be that progressively increasing hydrophobic interaction between links of a PVP chain occurs with increasing $\bar{P}$ in going from oligomer to polymer, and there is an accumulation of hydrophobic groups on the chain. The phenomenon of PVP link dehydration has been demonstrated

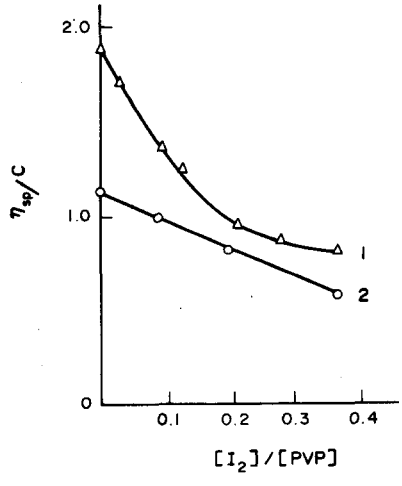

Fig. 6. Dependences of specific viscosity for PVP with $\bar{M}_n = 1.5 \cdot 10^6$ (1) and $3.5 \cdot 10^5$ (2) on [I_2] in aqueous solution. Experimental conditions: 25°, [PVP] = 0.1 g/dl.

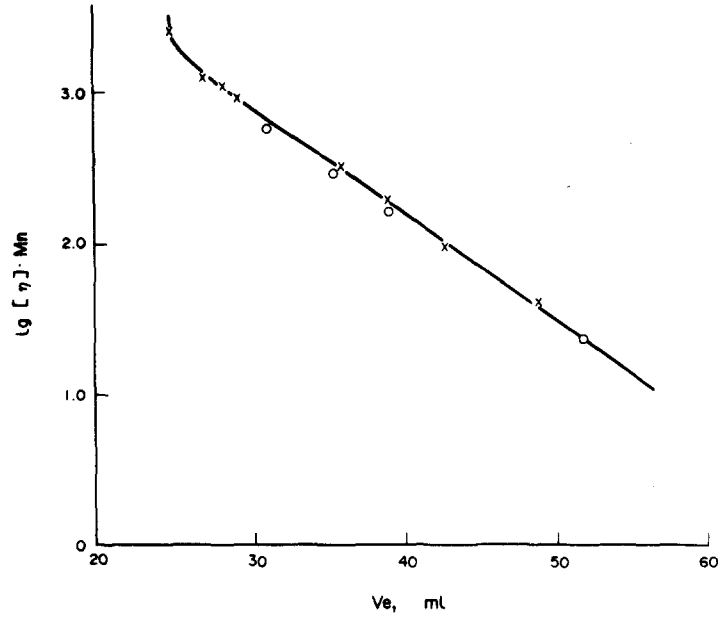

Fig. 7. Dependence of log ($[\eta]$ $\bar{M}_n$) on elution volume (V_e) for PVP (*——*) and polyethyleneglycol (O——O).

by the spin-lattice relaxation technique [23]. The link of PVP macromolecules was observed to be hydrated by about 15 water molecules, then the monomer molecule being surrounded by about 50 water molecules. Our finding of the considerable increase for the fluorescent intensity of ANS in PVP complexes indicates directly the hydrophobic environment of the probe created by PVP links. The partial dehydration seems to favour intensification of the electrostatic interaction for I_3^- and ANS anions with pyrrolidone dipoles on the chain, increasing the ability for complex formation for higher $\bar{P}$.

It is worth noting that complex formation for PVP and I_3^- is accompanied by a conformational change of coils. In other words, the polymer coils begin to shrink, decreasing the hydrodynamic volume. As seen in Fig. 6, the specific viscosity of PVP with $\bar{M}_w = 1.5 \cdot 10^6$ and $3.5 \cdot 10^5$ decreases with increasing $[I_3^-]$. At the same time, an increase of [KI] in the absence of I_2 has no effect on the specific viscosity. This fact indicates that molecules of I_3^- (or other formations for example I_5^-, I_7^-) associate with some links of a coil.

The PVP and polyacid interaction

PVP is known to complex with polyacids such as PAA and PMAA decreasing their hydrodynamic volumes [4]. In the present work the analytical fractionation of the PVP fraction was carried out and the specific viscosities of PAA and PMAA aqueous solutions were measured after adding extra fractionated PVP. The fractionation of the narrow fraction obtained by the preparative method was carried out using G-75 and G-50 sephadexes. The dependences of log ($[\eta] \cdot \bar{M}_n$) on V_e for PVP and PO were found (Fig. 7). As seen, these plots are sufficiently similar to allow estimation of PVP molecular weights near $\bar{M}_n \simeq 10^3$.

A change of viscosity for the polyacids when adding the PVP narrowest fraction with unlike $\bar{M}_n$ is presented in Fig. 8. The viscosity of PMAA decreases with decreasing $\bar{M}_n$, from $10 \cdot 10^3$ to $3 \cdot 10^3$, indicating PVP and PMAA complex formation. Since link concentrations for PVP with different $\bar{M}_n$ and that of PMAA are not changed, the viscosity fall for PMAA is due to increase of the concentrations for PVP macromolecules entering in the polymer complexes, PVP macromolecules with $\bar{M}_n$ in the above range being likely to interact equally to PMAA macromolecules. After adding the PVP fractions with $\bar{M}_n < 2.5 \cdot 10^3$, the PMAA viscosity begins to increase. This finding suggests a weakening for complex formation between PMAA and PVP with $\bar{M}_n$ below $2.5 \cdot 10^3$. The complexation ability for these macromolecules decreases over the range of $\bar{M}_n$ from $2.5 \cdot 10^3$ to ~ 300.

A similar effect was observed for PAA. In this case, unlike PMAA, a threshold value of molecular weight of PVP below which the interaction begin to weaken, is $6 \cdot 10^3$. Threshold values of $\bar{M}_n$ and numbers of bonds (N) for PVP macromolecules are presented in Table 1.

It is worth noting that these values remain unchanged on varying the molar ratios for the polymers and fractions (Fig. 8). Similar measurements were carried out using polyethyleneglycol after fractionating commercial samples (Table 1).

Comparison of the threshold values indicates unlike complexation capabilities of PAA and PMAA. In the case of PMAA, the polymer complex formation appears to be intensified by hydrophobic interactions between nonpolar regions of two macromolecules (PVP and PMAA) apart from hydrogen bonds. One can conclude also that PO macromolecules with polyacids associate less than PVP. Addition of PVP oligomers with $\bar{M}_n$ = 300–500 affect insignificantly the viscosities of the polyacids, indicating a loss of their capability to interact with PAA and PMAA under the studied conditions.

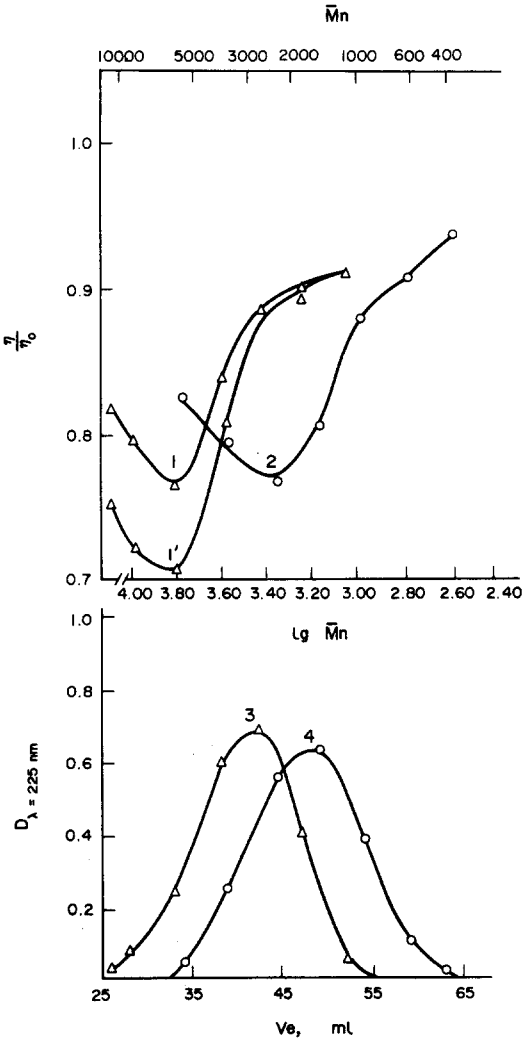

Fig. 8. Dependence of ratio for specific viscosity PAA ($\bar{M}_w = 5 \cdot 10^5$) (1,1') and PMAA ($\bar{M}_w = 3 \cdot 10^5$) (2) in the presence of PVP to that of these polyacids on PVP molecular weight. Experimental conditions: 25°, PVP fractions with $\bar{M}_n$ $2.4 \cdot 10^3$ (3) and $1.6 \cdot 10^3$ (4), [PVP] = $2.3 \cdot 10^{-5}$M (1), $1.0 \cdot 10^{-4}$M (1',2), [PAA] = $1.2 \cdot 10^{-2}$M (1), $1.5 \cdot 10^{-2}$M (1'), [PMAA] = $1.3 \cdot 10^{-2}$M (2).

Table 1. Threshold values of $\bar{M}_n$ and numbers of bonds (N) for PVP and polyethylenglycol (PO) interacting with polyacids

Polyacids	PVP		PO	
	$\bar{M}_n$	N_t	$\bar{M}_n$	N_t
PAA				
$\bar{M}_w = 3 \cdot 10^5$	$6 \cdot 10^3$	110	$6 \cdot 10^3$	400
PMAA				
$\bar{M}_w = 5 \cdot 10^5$	$2.5 \cdot 10^3$	45	$3 \cdot 10^3$	200

Thus, the study of a PVP fraction with low and high molecular weight compounds permits determination of the molecular weight at which there is the most marked change of PVP capability to the complex formation.

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