BEHAVIOUR OF POLYPYRROLIDONE
IN A MIXTURE CALCIUM CHLORIDE/ETHANOL/WATER

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The solution behaviour of polypyrrolidone was investigated in a ternary solvent $CaCl_2$/water/ethanol. The intrinsic viscosity increases with increasing concentration of ethanol and decreases with increasing concentration of calcium chloride. The constants of the Mark-Houwink equation ($a = 0.57$, $K = 10.7 \cdot 10^{-4}$) and the characteristic ratio of unperturbed dimensions of the polypyrrolidone chain (6.5) were determined in the mixture 3 g $CalCl_2$/10 ml (H_2O/35 vol.% ethanol). Positive selective sorption of the salt on the polymer was also detected in this mixture.

Polypyrrolidone dissolves in usual solvents of other polyamides, such as phenols, halogenated alcohols, strong acids or aqueous solutions of inorganic salts[1]. An investigation of the solution properties (*e.g.*, determination of the molecular parameters) requires that the polymer should be dissolved molecularly in the given solvent and that it should not degrade. In addition to this, specific requirements complying with the method used (boiling point, refractive index, hygroscopicity *etc.*) must be respected when choosing the solvent. Thus, 2,2,3,3-tetrafluoropropanol with 50 vol.% of water was chosen for the determination of the molecular weight of polypyrrolidone by the light scattering method, while *m*-cresol was selected for viscometric measurements[1,2].

The polymer processing from solution calls for the choice of the solvent according to other criteria, such as price, toxicity, corrosiveness *etc.* Since phenols and halogenated alcohols are quite expensive and acids affect polypyrrolidone hydrolytically, aqueous solutions of inorganic salts seem suitable for wet processing. From this standpoint Japanese authors[3] investigated dilute and concentrated solutions of polypyrrolidone in concentrated solutions of $ZnCl_2$ (also in a mixture with some other salt, such as $MgCl_2$, $CaCl_2$ *etc.*). They found that the solutions were stable at room temperature (the polymer degraded above 30°C) and that the intrinsic viscosity of polypyrrolidone in such solvent systems was considerably lower than in cresol.

It has been the objective of this work to examine the solution behaviour of polypyrrolidone in the mixture $CaCl_2/H_2O/C_2H_5OH$ and to compare it with the behaviour in other solvents with respect to the quality of the solvent and to the conformational rigidity of the polypyrrolidone chain.

EXPERIMENTAL

Three unfractionated samples (M_w 45·5 . 10^3, 64·5 . 10^3, 125 . 10^3) and seven fractions (9 . 10^3 to 155 . 10^3) of polypyrrolidone were used in the experiments. The polymer preparation and fractionation have been described earlier[2]. 2,2,3,3-Tetrafluoropropanol (further TFP), produced by Schuchardt, Munich, was rectified and its purity was checked chromatographically.

The molecular weights of polypyrrolidone were measured by the light scattering method with a SOFICA apparatus in 2,2,3,3-tetrafluoropropanol/50 vol.% water as a mixed solvent[2]. The intrinsic viscosity was measured at 25°C with an Ubbelohde viscometer by using the standard procedure. Measurements of the refractive index increments of the polymer at a constant concentration and a constant chemical potential of the components of the mixed solvent using differential refractometry and dialysis have been described earlier[4].

RESULTS AND DISCUSSION

Solubility of Polypyrrolidone in the Mixture $CaCl_2/H_2O/C_2H_5OH$

Polyamide 66 is known to dissolve readily in alcoholic solutions of $CaCl_2$; water added to this system reduces the solubility of the polymer[5]. Polypyrrolidone is insoluble both in an aqueous and in an alcoholic solution of $CaCl_2$, and can be dissolved only in an aqueous solution of $CaCl_2$ with $ZnCl_2$ added[3]. We found that polypyrrolidone could be dissolved in an aqueous–ethanolic solution of $CaCl_2$. The composition range of the solvent mixture in which we were able to prepare an at least 1% polypyrrolidone solution stable at 25°C is shown in Fig. 1. While in mixtures whose composition is close to the centre of the hatched region it is possible to prepare stable solutions of polypyrrolidone at a concentration of several tens per cent, in mixtures near the periphery of the hatched region the polymer in solution having a concentration of several per cent precipitates after a few hours.
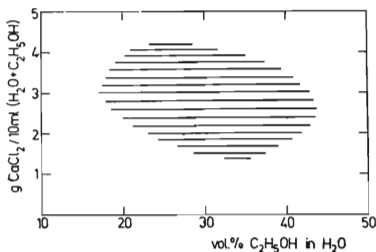

FIG. 1

Range of Solubility of Polypyrrolidone in the Mixture $CaCl_2/H_2O/C_2H_5OH$

In order to obtain a preliminary estimate of the dependence of the quality of the solvent mixture on its composition, we determined the intrinsic viscosities of the polypyrrolidone sample at a constant concentration of $CaCl_2$ and different water/ethanol ratios, and also at a varying concentration of $CaCl_2$ and a constant water/ethanol ratio (Figs 2a, 2b). It can be said that the thermodynamic quality of the solvent (intrinsic viscosity being its measure in the first approximation) decreases with increasing concentration of $CaCl_2$ and increases with increasing concentration of ethanol. On the contrary, for aqueous solutions of $ZnCl_2$ an increase in the intrinsic viscosity of polypyrrolidone with increasing salt concentration was observed[3]. Similarly to aqueous solutions of $ZnCl_2$[3], we found for the mixtures $CaCl_2/H_2O/$ $.C_2H_5OH$ that the intrinsic viscosities of polypyrrolidone were three to five times lower than the corresponding values in *m*-cresol. Both the time and heat stabilities of dilute solutions of polypyrrolidone in the mixture $CaCl_2/H_2O/C_2H_5OH$ are very good, unlike the aqueous solutions of $ZnCl_2$[3]. A 5% decrease in the intrinsic viscosity was observed only after the polypyrrolidone solution had been heated at 90°C for 15 hours.

We tried to determine the molecular weight of several polypyrrolidone samples by the light scattering method in the mixture of 3 g $CaCl_2/10$ ml ($H_2O/35$ vol.%
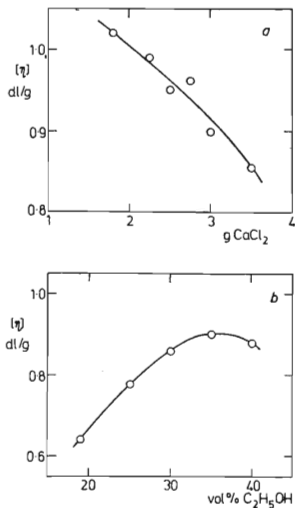

Fig. 2

Dependence of Intrinsic Viscosity of Unfractionated Polypyrrolidone on the Composition of the Mixture $CaCl_2/H_2O/C_2H_5$. .OH;

a) X-axis: g$CaCl_2$ per 10 ml ($H_2O/35$ vol.% C_2H_5OH; *b*) X-axis: vol.% C_2H_5OH in the mixture with water at constant concentration of $CaCl_2$ [3 g $CaCl_2/10$ ml ($H_2O/$ $/C_2H_5OH$)].

C_2H_5OH) using the refractive index increment determined after the establishment of the dialysis equilibrium between the polymer solution and the solvent. Although the molecular weights agreed with the values determined in the mixture TFP/50 vol.% water (which indicates that the polymer is molecularly dissolved), the aqueous-alcoholic solutions of calcium chloride cannot be recommended for the light scattering method because of the difficult and time-consuming optical purification of samples before measurement.

Relationship Between Intrinsic Viscosity and Molecular Weight

In order to determine the constants of the Mark-Houwink equation $[\eta] = KM^a$ of polypyrrolidone in the mixture of 3 g $CaCl_2$/10 ml (H_2O/35 vol.% C_2H_5OH), we measured the intrinsic viscosities of seven fractions and three unfractionated samples, molecular weight $9 . 10^3 - 155 . 10^3$. The dependence log $[\eta]$ vs log $\dot M_w$ is linear (Fig. 3) and yields $K = 10 \cdot 7 . 10^{-4}$ and $a = 0 \cdot 57$. Comparison with a for m-cresol as solvent $(0 \cdot 77)$ and the mixed solvent TFP/10 vol.% H_2O $(0 \cdot 80)$ shows that the chosen mixture $CaCl_2/H_2O/C_2H_5OH$ is a poorer solvent.

From the intrinsic viscosity and molecular weight values we obtained the viscometric constant K_0 $(19 \cdot 6 . 10^{-4})$ using the Stockmayer–Fixman plot $[\eta]/M^{1/2}$ vs $M^{1/2}$. Since the condition[6] $1 < [\eta]/K_0M^{1/2} < 1 \cdot 6$ was fulfilled, the equation $[\eta]/M^{1/2} = K_0 + CM^{1/2}$ was applied, where C is the proportionality constant (Fig. 4).
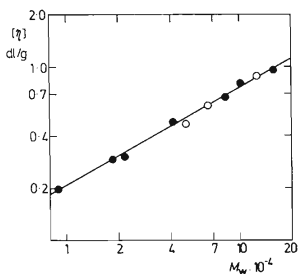
FIG. 3

Dependence of Intrinsic Viscosity on Molecular Weight of Polypyrrolidone in the Mixture 3 g $CaCl_2$/10 ml (H_2O/35 vol.% C_2H_5.OH).
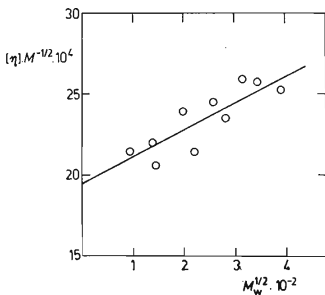
○ Unfractionated samples, ● fractions.

FIG. 4

Determination of the Viscometric Constant K_0 of Polypyrrolidone in the Mixture 3 g $CaCl_2$/10 ml (H_2O/35 vol.% C_2H_5OH)

K_0 was used to calculate the characteristic ratio of unperturbed dimensions, $\overline{r_0^2}/nl^2$:

$$\overline{r_0^2}/nl^2 = \left(\overline{r_0^2}/M\right)\left(m/l^2\right), \quad \overline{r_0^2}/M = \left(K_0/\Phi_0\right)^{2/3} ;$$

$\overline{r_0^2}$ is the mean square end-to-end distance, unaffected by the volume effect, nl^2 is the same quantity for a hypothetical "freely jointed" chain, Φ_0 is the Flory universal constant[7] $(2.6 \cdot 10^{21})$, M is molecular weight and m is the average weight per one skeletal bond. The value $l^2 = 0.0217$ nm^2 for polypyrrolidone was calculated from the bond lengths used in the calculation of the characteristic ratio of polycaprolactam[7]. Then, $m = 17.02$ and $\overline{r_0^2}/M = 0.827 . 10^{-16}$. The resulting value $\overline{r_0^2}/nl^2$ 6.5 for polypyrrolidone in the mixture 3 g CaCl$_2$/10 ml (H$_2$O/35 vol.% C$_2$H$_5$.OH) lies between the values for polypyrrolidone in the mixture TFP/10 vol.% H$_2$O (5.0) and in m-cresol $(7.5)^2$. In agreement with the expected dependence of unperturbed dimensions on the dielectric constant of the solvent[8] the characteristic ratio is lower in the mixture CaCl$_2$/H$_2$O/C$_2$H$_5$OH than in m-cresol. On the other hand, the value 6.5 is higher not only than that in the mixture TFP/H$_2$O, but also than that for polycaprolactam in the mixture TFP/H$_2$O $(6.07)^6$. We expected for polypyrrolidone that the characteristic ratio determined in a solvent having a high dielectric constant will be lower than for polycaprolactam, basing on the theoretically assumed[7] and experimentally proved fact[9] that the conformational rigidity of the polyamide chain decreases with increasing frequency of the amide groups. A higher characteristic ratio has also been observed for polycaprolactam in the mixture CaCl$_2$/methanol (9.41), where the authors[5] explain it by specific interactions between complexes CaCl$_2$–alcohol and the amide groups of polyamide.

Selective Sorption of CaCl$_2$ *on Polypyrrolidone*

Not much can be said about the nature of solvation of polypyrrolidone in the mixture CaCl$_2$/H$_2$O/C$_2$H$_5$OH, because spectroscopic methods, which could provide useful information, cannot be applied owing to the presence of water. One may assume that calcium with the coordination number 6 forms a complex with the molecules of water and ethanol[5], and that this complex is able to solvate the carbonyl group on the polymer chain by one of its coordination valencies. We attempted to prove the active role of calcium chloride in solvation (dissolution) of polypyrrolidone by determining its selective sorption on the polymer. The coefficient of selective sorption, γ, which is a measure of the difference between the concentration of the component under investigation inside and outside the polymer molecules, can be determined directly by using $\gamma = (v_\mu - v_c)/v_\phi$ where v_μ is the refractive index increment, measured from the difference between the refractive indexes of the polymer solution and of the solvent at a constant chemical potential of the solvent com-

ponents in solution and solvent, v_c is the same value determined for the constant concentration of the solvent components, and v_ϕ is the refractive index increment of that solvent component, whose γ we determine, in the absence of the polymer. For the sake of simplicity, in the determination of γ of calcium chloride we regarded $CaCl_2$ as one component, and water and ethanol as the other component of the mixed solvent used. Such simplification is possible owing to the small difference between the refractive indexes of water and ethanol against a very different refractive index of $CaCl_2$.

In the system 3 g $CaCl_2/10$ ml $(H_2O/35$ vol.% $C_2H_5OH)$ we obtained v_μ 0·177, v_c 0·128, v_ϕ 0·148 and γ 0·33. Consequently, a positive coefficient of selective sorption proves an increased concentration of $CaCl_2$ in polymeric coils. It still remains to be found out why in this solvent for polypyrrolidone (unlike polycaprolactam) both water and alcohol must necessarily be present at the same time.

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