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Effects of inorganic salts on the properties of aqueous poly(vinylpyrrolidone) solutions

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Abstract: Cloud point curves and θ temperatures have been determined for aqueous solutions of poly(vinylpyrrolidone) at several concentrations for a variety of inorganic salts (phosphates, monohydrogen phosphates, sulfates, carbonates, dihydrogen phosphates and fluorides). The resulting dependency of the critical temperatures θ (mostly between 289 and 350 K) on the molar concentration can be expressed as sequences showing the decreasing effect of anion species or cation species in salting out the polymer. The decreasing order of effectiveness of the anions in reducing the θ temperatures is $PO_4^{3-} > HPO_4^{2-} > SO_4^{2-} \approx CO_3^{2-} > H_2PO_4^- > F^-$. The order for cation is $Na^+ > K^+$. The changes brought about in θ temperatures by the salts were found to be the results of the changes taking place in the hydrophilic and hydrophobic interactions among polymer, solvent and additive salts and of the change of water structure by structure making or structure breaking ions, and of the influence of salts on the hydration sheath of the polymer.

Key words: Poly(vinylpyrrolidone) – cloud points – θ temperatures – effect of salts

Introduction

Poly(vinylpyrrolidone) (PVP) was synthesized from acetylene by Reppe and his associates [1] in 1939–41. In the course of their 50-year history vinylpyrrolidone polymers have been extensively used for numerous technical applications.

PVP contains a polar lactam group in an otherwise hydrophobic structure and it exhibits a series of interactions toward small dissolved molecules which were mentioned previously [2]. Solubility of PVP is extremely high in water and its solutions with certain salts added, are used in surgery. When PVP is dissolved in water, the polymer molecule is expected to be hydrated, and the hydrated polymer chain spreads out in aqueous media. PVP aqueous solutions is therefore considered to be hydrophilic colloid. Hydrophilic colloids are more stable than hydrophobic colloids and need high concentration of the electrolytes to be floccuated. By addition of electrolytes or elevation of temperature, hydrophilic colloids lose their water and dehydrated colloids begin to precipitate. When precipitation begins to take place PVP aqueous solutions becomes cloudy.

The cloud point temperature depends on the salt involved, its concentration and the concentration of the polymer. There is a correlation between the critical flocculation temperature (CFT) which is the minimum temperature at which flocculation is observed and the θ temperature. The determination of the theta conditions (in this study theta temperatures) is particularly of great concern from the steric stability point of view.

The studies of the interaction between polymers and additives have been carried out by different methods, equilibrium dialysis [3], solubility measurements [4] and viscometry [5], etc., but, these

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*) Deceased

methods require much time before the equilibrium is reached, or tend to give much error in the measurements. The cloud point method was therefore examined to evalute the interaction between PVP and some inorganic compounds.

The effects of inorganic salts on the cloud point temperatures of aqueous salt solutions of PVP were published by Molyneux [6] and Sekikawa, et al. [7]. The cloud point temperatures of PVP aqueous solutions lowerd linearly with increasing concentrations of salts.

Aqueous salt solutions of PVP exhibit a lower critical solution temperature (LCST) i.e., they cloud on heating in the range 288–358 K.

In the present study, the effects of inorganic salts over a range of concentrations on the cloud point curves, and the theta temperatures derived therefrom for poly(vinylpyrrolidone) have been investigated.

Experimental

The polymer samples used in this study were commercial BDH poly(vinylpyrrolidone), designated UF1 and UF2, both have nominal molecular weight, 44000 and 700000. The sample UF2 was fractionated by three-angular fraction method at 20 °C, using chloroform and petroleum ether (80 °C) as a solvent–nonsolvent pair. Originally four fractions were obtained and weight-average molecular weights of two fractionated and two unfractionated samples were determined by using a light scattering photometer. In this study, "Brice-Phoenix Light Scattering Photometer, 2000 Series" was used for measuring the Rayleigh ratios. The interpretation of light scattering data was based on the Zimm method, expressed in the general form;

$$K_c/R_\theta = 1/\bar{M}_w[1 + (16\pi^2/3\lambda^2) \times \langle S^2\rangle_z \sin^2\theta/2] + 2A_2C + \ldots$$

The results of light scattering measurements are given in Table 1.

Table 1. Light scattering measurement of PVP in chloroform at 30 °C and 436 nm

Sample	$\bar{M}_w \times 10^{-5}$ (g/mol)	$A_2 \times 10^4$ (cm^{3}mol/g)	$\langle S^2\rangle^{1/2} \times 10^{-2}$ (Å)	$[\eta]$*) (dl/g)
UF1	0.78	7.07	0.72	0.12
F3	2.64	6.17	1.83	0.62
UF2	5.48	5.17	3.28	0.93
F2	7.58	5.12	3.40	1.14

*) Viscosities were measured by using Ubbelohde viscometer in chloroform at the same temperature.

The number-average molecular weight of sample UF1 was determined by "Knauer Membrane Osmometer" and molecular weight distribution is found to be $\bar{M}_w/\bar{M}_n < 1.7$.

The determination of cloud point temperatures was carried out in pyrex tubes containing aqueous salt solutions of PVP; they were immersed in a well-controlled stirred and heated bath. The solutions were also stirred by a Teflon magnetic stirring bar while being heated. The first appearance of cloudy aqueous salt solutions of PVP was taken as cloud point temperature. Reproducibility of the cloud point measurements was excellent, within the range ± 0.1 °C.

All the inorganic salts were of reagent grade. The salts and the polymer samples were dried in vacuum at 40 °C and they were stored in a desicator which contained P_2O_5.

Results

Cloud points

The polymer solutions which contain inorganic salts become cloudy on heating. Cloud point temperatures (T_{cp}) decrease on increase in the salt concentration. Trivalent anion is much more effective in decreasing the cloud point temperature of PVP than are the other univalent and divalent anions. The addition of some univalent salts, such as sodium and potassium formates, acetates, chlorides, and nitrates did not cause any cloud formation in the polymer solutions under the experimental conditions (at atmospheric pressure and to 368 K) for UF1 sample, even the salts concentration was over 6 M.

The turbidimetric technique of Cornet and Ballegooijen [8] later developed by Talamani and Vidotto [9] and by Napper [10], is not dependent on the molecular weight and subsequently applied to a variety of systems. In this method, for determination of θ temperatures, assumes that the interaction parameter χ_1 and

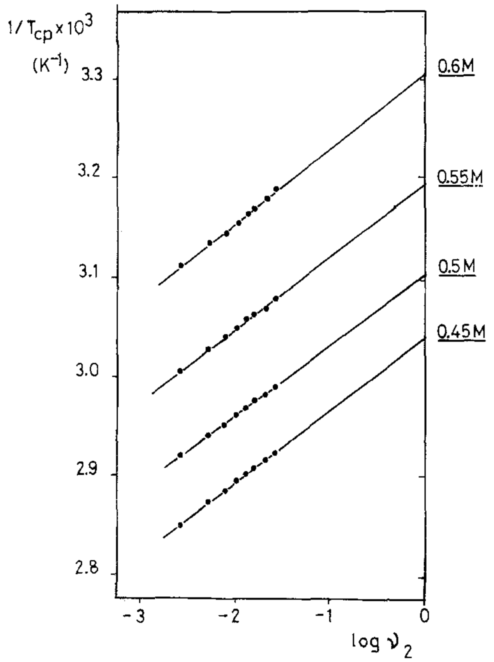

Fig. 1. Reciprocal of cloud point temperature $1/T_{cp}$ against log υ_2 for the molar concentration of K_2CO_3

log υ_2 have a linear dependence within the range of $-5 \leqq \log \upsilon_2 \leqq -2$. This is verified by the straight line graph of T_{cp}^{-1} versus log υ_2 and the intercept of this line gives $1/\theta$ at log $\upsilon_2 = 0$. As an example, the reciprocal of cloud point temperature of potassium carbonate can be seen in Fig. 1. The θ temperatures of UF1 polymer sample (given in Table 2A) for various inorganic salts are determined by linear regression analysis similar to the results shown in Fig. 1.

The reciprocal of cloud point temperatures, $1/T_{cp}$ of phase separation of two fractionated and two unfractionated PVP samples have also been plotted as a function of $1/\bar{M}_w^{1/2}$. The θ temperatures in four different salts were calculated by extrapolating to infinite molecular weight. The results of the cloud point temperatures with the different molecular weight of PVP salt solutions are shown in Fig. 2, and the θ temperature values are also mentioned in Table 2B. It is observed that two procedures give the same θ temperatures for PVP in aqueous salt solutions. The θ temperature of PVP in 0.55 M Na_2SO_4 solution is reported as 301 K by Meza and Gargallo [11] by using this second method.

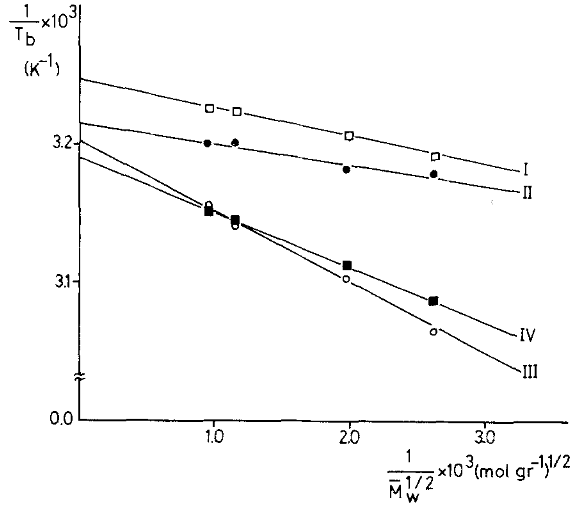

Fig. 2. Reciprocal of cloud point temperature $1/T_{cp}$ of four poly(vinylpyrrolidone) samples as a function of $1/\bar{M}_w^{1/2}$

The relation between θ temperatures and the molar concentration of salt for univalent, divalent, and trivalent anion salts is shown in Fig. 3. The major features to be noticed are that:

1) The salts of trivalent phosphate ion have the greatest effect on the suppression of T_{cp} and θ temperatures for sodium and potassium salts.
2) The salts of divalent monohydrogen phosphate have greater effect than the other divalent anions.
3) Two other divalent anions, sulfates and carbonates exhibit almost the same behavior on the suppression of T_{cp} and θ temperatures.
4) And, the salts of univalent dihydrogen phosphate and fluoride have the smallest effect on the general behavior.

The θ temperature of PVP in water is found to be about 420 ± 7 K by the extrapolation to the zero salt concentration of the curves of θ temperatures versus molar salt concentration for various salts in Fig. 3. The θ temperature of PVP in pure water is in agreement with that found, $\theta = 413 \pm 5$ K previously [11].

Salt effects

In neutral or weak alkaline solutions the order of effectiveness of various ions in salting out, on

Table 2. Theta temperatures (K) of aqueous poly(vinylpyrrolidone) solutions at various molar salt concentrations
A. UF1 poly(vinylpyrrolidone) sample

Na_3PO_4		K_3PO_4		Na_2HPO_4		K_2HPO_4	
C_3	θ	C_3	θ	C_3	θ	C_3	θ
0.20	346	0.25	344	0.25	342	0.35	339
0.25	330	0.30	334	0.30	327	0.40	328
0.30	309	0.35*	313	0.35*	308	0.45	313
0.35	289	0.40	302	0.40	295	0.50	306

Na_2SO_4		K_2SO_4		Na_2CO_3		K_2CO_3	
C_3	θ	C_3	θ	C_3	θ	C_3	θ
0.35	346	0.45	326	0.40	333	0.45	329
0.40	335	0.50	317	0.45	322	0.50	323
0.45	321	0.55	307	0.50*	312	0.55	313
0.50	309	0.60	295	0.60	293	0.60	302

NaH_2PO_4		KH_2PO_4		Li_2SO_4		KF		$(NH_4)_2SO_4$	
C_3	θ	C_3	θ	C_3	θ	C_3	θ	C_3	θ
0.80	367	0.80	350	0.70	332	0.90	338	0.60	323
0.90	328	0.90	337	0.80	315	1.00	328	0.65	312
1.00	319	1.00	330	0.90	306	1.10	318	0.70	303
1.10	308	1.20	308	1.00	293	1.20*	311		

B. With UF1, F3, UF2 and F2 polymer samples

Salts		C_3	θ
K_3PO_4	(IV)*	0.35	313
Na_2HPO_4	(I)*	0.35	308
Na_2CO_3	(III)*	0.50	312
KF	(II)*	1.20	311

The errors introduced in θ temperatures are ± 1 K and correlation coefficients are 0.997 ± 0.001 (except 0.3 M K_3PO_4) (*, in Fig. 2)

the suppression of T_{cp} and θ temperatures, of PVP aqueous salt solutions was found to be:

i) For the sodium anions,

$$PO_4^{3-} > HPO_4^{2-} > SO_4^{2-} \approx CO_3^{2-} > H_2PO_4^-$$

ii) For the potassium anions,

$$PO_4^{3-} > HPO_4^{2-} > SO_4^{2-} \approx CO_3^{2-} > H_2PO_4^- > F^-$$

on the basis of molar concentrations.

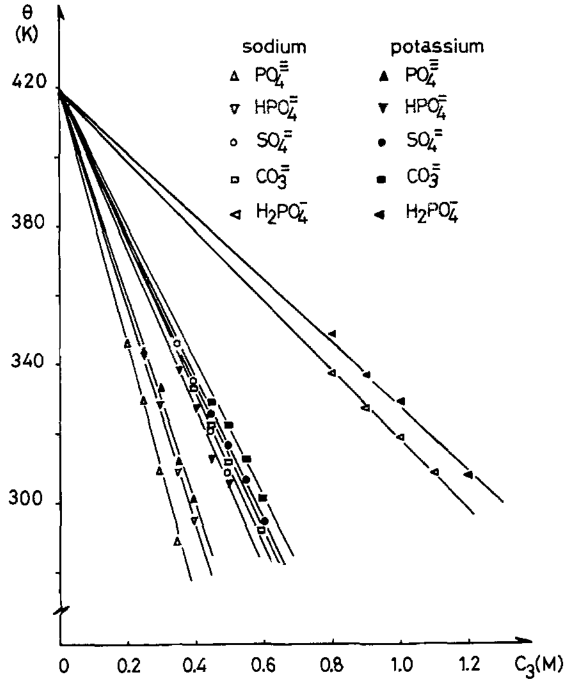

Fig. 3. Dependence of theta temperatures on molar concentration of sodium and potassium salts

The cloud points of PVP aqueous solutions were measured with the addition of some sodium salts by Sekikawa and co-workers [7] as a function of molecular weight of polymer and in the presence of some different types of additives. The series for sodium anions in decreasing order of effectiveness in coacervation of PVP (M.W = 3.6×10^5) in aqueous salt solutions was found to be:

Tribasic sodium phosphate > dibasic sodium phosphate > monobasic sodium phosphate, on the basis of molar concentrations.

PVP has the ability to bind reversibly to small molecules forming association complexes which are important from points of view, in chemistry, biochemistry and pharmaceutical sciences. Especially, the existing similarities between the chemical structures of PVP and proteins have led to proposals for PVP as a synthetic polymer model for proteins [12, 13]. Hofmeister have investigated the precipitation of proteins in the presence of salts and the Hofmeister sequence of decreasing effect in reducing T_{cp} for anions incorporating some of the previous results can now be extended on molar concentration basis as follows,

$$PO_4^{3-} > HPO_4^{2-} > SO_4^{2-} \approx CO_3^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > HCOO^- > CH_3COO^- > Cl^{-1} > NO_3^- > Br^- > I^- .$$

The cation sequence depends on the kind of anion, especially for the relative places of sodium and potassium ions. Henceforth, the cation sequence of decreasing salting out power for PVP in aqueous solutions of phosphates can be shown as $Na^+ > K^+$. But it seems impossible to state a precise sequence with all the cations, especially with the cations Li^+ and NH_4^+. Previously, certain irregularities were also observed for PVP in aqueous salt solutions [7]. The order for the cations has been reported as, $Na^+ \approx K^+ \approx Rb^+ \approx Cs^+ > NH_4^+ > Li^+$ of aqueous salt solutions of poly(ethyleneoxide) (PEO) [14].

The anion sequence found in this work for PVP, and the sequence reported by Ataman [14] for PEO shows a great similarity. Ataman's sequence for anions (sulfates and carbonates were not studied) in decreasing order of effectiveness in salting out of PEO in aqueous salt solutions was found to be:

$$PO_4^{3-} > HPO_4^{2-} > S_2O_3^{2-} > H_2PO_4^- > F^- > HCOO^- > CH_3COO^- > Br^- > I^-$$

on the basis of molar concentrations. It is observed that the anion sequences found in PVP and PEO salt solutions are almost the same. Is the salting out phenomena related to the polymer structure or not? The authors believe that this point needs to be investigated experimentally.

Discussion

The effects of salt species in aqueous salt solutions of PVP and the suppression of the cloud point temperature of PVP as a combination of several effects i.e., the interaction of the polymer with the solvent, or the binding of the water molecules to polymer, or a kind of molecular association [15], change in the water structure, and in the hydration sheath due to the added salt could be discussed. It is known that the addition of an electrolyte to water changes the hydrogen-bonded structure of water. The model of Frank and Wen [16] for aqueous salt solutions still provides a basis for discussing water, which is supposed to consist of three regions. Region A, the innermost region of polarized bound water molecules around the ion. Region B, comprising water molecules partially ordered by the electric field of the ion and region A. Region C, where intermolecular hydrogen bonding occurs as in bulk water. The proportion B can be considered as one where the normal hydrogen-bonded structure has been destroyed, and the physical extent of B relative to A and C is a measure of the structure-breaking ability of the species of central ion. Depending on whether the ion is a structure breaker or not the normal hydrogen-bonded structure of water is either destroyed or retained.

The clouding of aqueous salt solutions of PVP is associated with changes in the normal structure of water induced by electrolytes. Verrall's [17] anion sequence, and James and Frost's [18] studies for the decreasing ability to destroy the hydrogen-bonded structure of water based on IR, and Hindman's [19] anion sequence based on NMR techniques are in general agreement with the trends found above. By viscometric studies, Puett and Rajagh [20] have reported that the sulfate ion is a more effective structure breaker than fluoride ion. The monovalent anions follow the structure making sequence, and, in this respect, the fluoride ion is the most effective in salting out phenomena. On the other hand, in the case of divalent and trivalent anions the salting out power cannot be explained solely by structure making ability of the anion. Since PVP is typical hydrophilic polymer, their effectiveness may originate in electrostatic artefacts.

The sequence of cations for the decreasing structure breaking ability [16, 17] is in harmony with the decreasing salting out ability of cations. The more structure breaking the cations are, the more effective they are in salting out.

In the case of PVP structure, polymer contains N–C = O units on the lactam rings, and these polar groups are involved for the association with water molecules by hydrogen bonding. The association of lactam units (especially, with the unshared electron pairs of carbonyl) of PVP with water has been observed both by viscometric measurements [15] and spectrophotometric studies [2]. Hydration sheath of PVP is also investigated by Kobyakov et al. [21] in solution and hydrated polymer films by IR spectroscopy.

The addition of salts into aqueous solutions of PVP changes the association and/or hydration, and could cause a disruption of highly oriented water which surrounds the polymer. Consequently, the increasing hydrophobic behavior of the PVP chain should result in a lowering of the polymer precipitation temperature. Ise et al. [22] proposed that the PVP molecule might be present in the aqueous solutions with hydrophobic hydration around its polymer chain. Inorganic salt might compete with PVP molecules in hydration, and PVP molecule start to precipitate from solution. The effects of various ions on the association of polymer or the hydration sheath of PVP would be different, and can be explained on the basis of exclusion or ion changing studies, and by using spectrophotometric methods [23].

Compounds which interact with PVP molecule in aqueous solution, might release water which is hydrating PVP molecule. The configuration of PVP polymer chain may shrink when these compounds and PVP molecule interact [24]. One should also note that some other responsible factors, such as ion-dipole interactions should be considered, and probably the original structure of the pyrrolidone ring will have been changed in the presence of ions.

Furthermore, we suggest that there is a hydrogen bonding between weak acids formed in the hydrolysis of sodium and potasium formates, acetates in solutions, and those probably screen the interaction of PVP with the anions of $HCOO^-$ and CH_3COO^- in solution. Similar hydrogen bonding might exist in the aqueous solutions of the phosphate, monohydrogen phosphate and dihydrogen phosphate anions.

With the salts used in this study we have not observed any gel formation, except for the case of $K_2S_2O_8$ and $Na_2S_2O_8$ salts. It is probably due to the fact that direct binding of the polyvalent ions cause a gel formation in the mixture.

The effect of salts on the suppression of the cloud point temperature of PVP in aqueous solution appears to be a combined cation/anion effect, but the anion effect seems to be predominant. It is clear from the foregoing discussion that the salt effect on the suppression of the cloud point temperature of polymers in aqueous solutions depends on the polymer structure, and how the trends variously relate in detail to one to another in the analyzing of salt effects is currently rather qualitative. Continuing experimental studies and more diverse data should assist in developing a comprehensive theory.

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