

# Properties of Aqueous Salt Solutions of Polyvinylpyrrolidone. I. Viscosity Characteristics

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## SYNOPSIS

The properties of dilute solutions of polyvinylpyrrolidone (PVP) in aqueous salt solutions have been studied by measurements of intrinsic viscosity  $[\eta]$  in theta and nontheta solvents. Intrinsic viscosities of the polymer solutions were observed to decrease upon addition of a variety of inorganic salts (phosphates, monohydrogen phosphates, carbonates, sulfates, and dihydrogen phosphates). Values of the Huggins constant,  $k_H$ , were found to be higher than 0.35 for PVP in pure water at 298 K, whereas in salt solutions they varied from 0.85 to 1.28 in nontheta solvents. Kraemer's constant,  $k_K$ , was also determined and  $k_H - k_K$  was calculated as 0.78 for PVP in pure water and for aqueous salt solutions of PVP,  $k_H - k_K = 0.61$  at 298 K.  $k_H$  values were also higher than the predicted range of 0.5–0.7, and  $k_H - k_K$  values were noted to be 0.73 in theta solvents. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Aqueous salt solutions of polyvinylpyrrolidone (PVP) exhibit lower critical solution temperature (LCST) and theta temperatures in aqueous salt solutions, depending on the nature and concentration of the salt. Theta temperatures for a variety of inorganic salts (phosphates, monohydrogen phosphates, sulfates, carbonates, dihydrogen phosphates and fluorides) have been obtained from cloud-point temperatures.<sup>1</sup>

PVP is readily soluble in water. The solubility is only restricted by a sharp increase of the viscosity with increasing concentration. Although the polymer is easily soluble in water, the results of viscosimetric investigations verify that water is not a thermodynamically good solvent for PVP.<sup>2–4</sup>

The exponent  $\alpha = 0.55$  of the Kuhn–Mark–Houwink–Sakurada equation for the system PVP/H<sub>2</sub>O is close to 0.50, which is characteristic for theta solvents.<sup>5</sup> This is probably due to the following types of interactions that can take place in aqueous PVP solutions: (1) hydrogen bonds between the cyclic tertiary amid group of PVP and the protons of the solvent, and (2) hydrophobic interactions between hydrocarbon groups (cyclic methylene groups and those in the backbone).

Polymer–solvent interaction via hydrogen bonds must lead to a swelling of the polymer coils, and the hydrophobic interactions to compression, i.e., these two effects compensate each other.

The change in the enhanced water structure around the polymer caused by the added salt is expected to play an important role in the solution characteristics of PVP.

The influence of different salts and acids on the viscosity of PVP has also been investigated.<sup>6</sup> It has been shown that the addition of glycine and alanine decreases the intrinsic viscosity of PVP in water, whereas salts exhibit different influences on the viscosity. Thus, addition of NH<sub>4</sub>Cl does not change the  $[\eta]$ , whereas NaCl and NaClO<sub>4</sub> greatly decrease  $[\eta]$  and KSCN increases the intrinsic viscosity of PVP. It is also noted that tetraborate, diphosphate, and sulfate decreases  $[\eta]$  more strongly than do chlorides and chlorates.

In this study, the viscosity behavior of PVP in aqueous salt solutions was studied at 298 K and at the theta temperatures, and viscosity characteristics  $k_H$ ,  $k_K$ , and  $[\eta]$  were evaluated.

## EXPERIMENTAL

The polymer sample used in this study was commercial BDH PVP, and has a nominal molecular

**Table I** Viscosity Data for Aqueous Salt Solutions of PVP

$c_3$ (M)	Salt	$T$ (K)	$k_H^a$	$k_K$	$k_H - k_K^a$	$[\eta]$ (dL g <sup>-1</sup> ) <sup>a</sup>
1.20	NaH <sub>2</sub> PO <sub>4</sub>	298	0.973	0.365	0.608	0.155
		308 <sup>b</sup>	1.987	1.251	0.736	0.147
1.10	KH <sub>2</sub> PO <sub>4</sub>	298	1.019	0.412	0.607	0.160
		308 <sup>b</sup>	1.861	1.120	0.741	0.149
0.50	Na <sub>2</sub> SO <sub>4</sub>	298	0.854	0.245	0.609	0.169
		309 <sup>b</sup>	2.160	1.445	0.715	0.129
0.50	Na <sub>2</sub> CO <sub>3</sub>	298	1.074	0.471	0.603	0.162
		312 <sup>b</sup>	2.604	1.872	0.732	0.155
0.55	K <sub>2</sub> CO <sub>3</sub>	298	1.079	0.473	0.606	0.170
		313 <sup>b</sup>	2.274	1.546	0.728	0.138
0.35	Na <sub>2</sub> HPO <sub>4</sub>	298	1.286	0.681	0.605	0.145
		308 <sup>b</sup>	2.220	1.496	0.724	0.144
0.45	K <sub>2</sub> HPO <sub>4</sub>	298	1.028	0.422	0.606	0.161
		313 <sup>b</sup>	2.164	1.434	0.730	0.134
0.50	K <sub>2</sub> HPO <sub>4</sub>	298	1.122	0.514	0.608	0.151
		306 <sup>b</sup>	2.436	1.718	0.718	0.138
0.30	Na <sub>3</sub> PO <sub>4</sub>	298	1.163	0.557	0.606	0.162
		309 <sup>b</sup>	1.457	0.724	0.733	0.145
0.35	K <sub>3</sub> PO <sub>4</sub>	298	1.049	0.444	0.605	0.176
		313 <sup>b</sup>	2.414	1.689	0.725	0.152

<sup>a</sup> Checked by eqs. (3–7) (correlation coefficients are  $0.997 \pm 0.001$ ).

<sup>b</sup> Theta temperatures.

weight of 44,000. Weight-average molecular weight of polymer sample was determined by using a light-scattering photometer. In this study, a 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

$$K_c/R_\theta = 1/M_w[1 + (16\pi^2/3\lambda^2) \langle s^2 \rangle_Z \sin^2\theta/2] + 2A_2C +$$

It has a weight-average molecular weight,  $M_w = 78,000 \text{ g mol}^{-1}$  determined in chloroform at 298 K.

The number-average molecular weight of polymer was also determined by Knauer Membrane Osmometer, and molecular weight distribution was found to be  $M_w/M_n < 1.7$ .

Viscosity measurements were made by using an Ubbelohde capillary viscometer at 298 K, and at the theta temperatures previously determined.<sup>1</sup> Temperatures were controlled within  $\pm 0.02^\circ\text{C}$  and flow times were measured with an accuracy of  $\pm 0.1$  s. Deionized and twice distilled water was used for the preparation of solutions. The concentration of PVP ( $c_2$ ) in aqueous salt solutions was changed in the range of 0.4–1.0 g dl<sup>-1</sup>. The effect of the shear rate was ignored because the molecular weight of the

polymer was not too high. All the inorganic salts were of reagent grade.

## RESULTS AND DISCUSSION

### Viscosity Characteristics

The intrinsic viscosities  $[\eta]$  and  $[\eta]_\theta$  were evaluated as average values of the intercepts of the plots of  $\eta_{sp}/c_2$  vs.  $c_2$ . Straight lines were obtained when results for the dependence of specific viscosity ( $\eta_{sp}/c_2$ ), on polymer concentration ( $c_2$ ) at a particular salt concentration  $c_3$  were plotted according to

$$\eta_{sp}/c_2 = [\eta] + k_H[\eta]^2 c_2 \quad (1)$$

where  $k_H$  is the Huggins constant.<sup>7</sup>

Likewise, relative viscosities ( $\eta_{rel}$ ) are linearly related by

$$(\ln \eta_{rel})/c_2 = [\eta] + k_K[\eta]^2 c_2 \quad (2)$$

where  $k_K$  is the Kraemer's constant.<sup>8</sup> Table I gives the  $k_H$  and  $k_K$  from slopes, and intrinsic viscosities  $[\eta]$  from intercepts where  $c_2 = 0$ .

Another equation is presented by Maron and Reznik<sup>9</sup> for determination of the intrinsic viscosity

of partially concentrated polymer solutions ( $> 0.5$  g dL<sup>-1</sup>).

$$\Delta = \eta_{sp} - \ln \eta_{rel} \quad (3)$$

$$\Delta = ([\eta]^2 c_2^2 / 2) + (k_H - \frac{1}{3})[\eta]^3 c_2^3 \quad (4)$$

Division of both sides of eq. (4) by  $c_2^2$  yields

$$\Delta / c_2^2 = ([\eta]^2 / 2) + (k_H - \frac{1}{3})[\eta]^3 c_2 \quad (5)$$

Equation (5) predicts that a plot of  $\Delta / c_2^2$  vs.  $c_2$  should be a straight line with intercept,  $I$ , given by

$$I = [\eta]^2 / 2 \quad (6)$$

And the slope,  $S$ , of the plot should be

$$S = (k_H - \frac{1}{3})[\eta]^3 \quad (7)$$

From eqs. (6) and (7), both  $[\eta]$  and  $k_H$  can be found easily.

Intrinsic viscosities of PVP in aqueous solution were calculated as 0.213, 0.217, and 0.213 dL g<sup>-1</sup> from eqs. (1), (2), and (3-6), and  $k_H = 1.316$  [eq. (1)],  $k_K = 0.536$  [eq. (2)], and  $k_H = 1.309$  [eq. (7)] at 298 K.

### Huggins Constant

For flexible polymer molecules,  $k_H$  is expected to be about 0.35 in good solvents and higher in poor solvents. The difficulty of interpreting the Huggins constant for polymer molecules is more involved because of the interpenetration of polymer coil. The extent of this penetration is a function of the polymer-polymer (or segment-segment) and polymer-solvent interactions, which affect the intramolecular hydrodynamic interaction and molecular dimensions.<sup>10</sup>

In some polymer-solvent systems, the Huggins constant assumes high values<sup>11-13</sup> that do not fit within the framework of the ideas presented in the preceding discussion, and which are usually referred to as molecular association. Molecular association of PVP in aqueous solutions and the effects of some denaturing agents were studied by Güven and Eltan<sup>14</sup> by the viscometric method, and the main responsible factor of these interactions were reported as "hydrogen bond" formation between water molecules and PVP side groups. The forming of hydrogen bonding and

association complexes with various solvents (aqueous and nonaqueous) were also studied by ourselves<sup>15</sup> spectrophotometrically for the same polymer.

The high  $k_H$  values found for aqueous solutions of PVP may be a result of the strong interactions of lactam groups of polymer with water molecules in solution by hydrogen bonding. Value of  $k_H - k_K = 0.78$  is higher than the expected value of 0.5 at 298 K. On the other hand, the  $k_H$  values found for aqueous salt solutions of PVP were smaller than PVP aqueous solution, and  $k_H - k_K$  value was calculated to be 0.606 ( $\pm 0.003$ ) at the same temperature (see Table I).

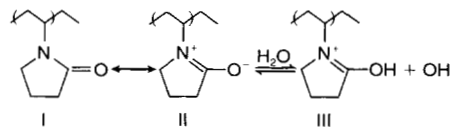
This supports the idea that the  $k_H$  value is a consequence of polymer-solvent interaction, rather than a measure of the solvent power.

The addition of certain salts to solution affects the hydrogen-bonded structure of water<sup>16</sup> and the strength of hydrogen bonding between polymer and solvent depending on the nature of the salt. Furthermore, some other types of interactions, such as, ion-lactam ring electrostatic interactions may exist in the solution.

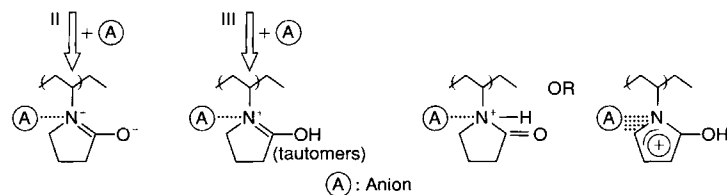
It has been known for many years that PVP exhibits a series of interactions toward small dissolved molecules and forms complexes with a variety of small molecules such as iodine,<sup>17</sup> triiodide,<sup>18</sup> azo dyes,<sup>19-21</sup> sodium dodecyl sulfate,<sup>22</sup> some aromatic compounds,<sup>23,24</sup> 2-p-toluidinylnaphthalene-6-sulfate,<sup>25</sup> and methyl orange and its homologues.<sup>26-28</sup> These studies revealed that both electrostatic and hydrophobic interactions are operative in the binding of PVP.

Klotz and Shikawa<sup>20</sup> studied the binding of methyl orange with serum albumin and PVP, and found that the binding affinity of PVP was one-third that of serum albumin. PVP, like serum albumin, showed a decreasing affinity for small molecules of different charge in the order of anions  $>$  neutral molecules  $>$  cations.

The following scheme proposed by Takagishi and Kuroki<sup>21</sup> should be noted here:



Because nitrogen possesses a partial positive charge, the most probable, electrostatic interactions between the nitrogen atom (or ring) and the anion could be as follows:



Electrostatic interactions between positively charged nitrogen atom and anion, binding of the ions (cations,  $\text{Na}^+$  and  $\text{K}^+$ , are more difficult to substantiate in aqueous systems), or of water molecules to the polymer and aggregation of polymer molecules may be responsible for the high  $k_H$  values.

Sakai<sup>29</sup> contends that because nonpolar polymer and solvent combinations for theta conditions should lie between 0.5 and 0.7,  $k_H$  may also be influenced by the aggregation of the polymer in solution. According to the calculations performed by Riseman and Ullman,<sup>30</sup> the Huggins constant under theta conditions should be equal to 0.6.

Vasudevan and Santappa<sup>31</sup> found  $k_H = 1.06$  for poly(ethylmethacrylate) under theta conditions (isopropanol, 310 K), and large values of Huggins constant (mostly  $> 1$ ) were found by Okada et al.<sup>32</sup> for polystyrene (in mixed theta solvents, methanol + toluene), and also by Newman et al.<sup>33</sup> for poly(acrylic acid) in theta solvent (dioxane at 303 K).

However, the values found in aqueous salt solutions of PVP are rather high compared to those in organic solvents.

Most of the  $k_H$  values found in this study were higher than the predicted range of 0.5–0.7, and  $k_H - k_K$  values were found to be  $0.730 \pm 0.015$  (Table I). In contrast to this increase of  $k_H$  in aqueous salt solutions, the value of  $[\eta]$  decrease relative to those in water. This shows that, with an increasing degree of hydrophobic interactions of polymer segments, the intramolecular association of the polymer coil increases, and, consequently, the polymer coil contracts.

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Received December 28, 1995

Accepted March 18, 1996