

# ***N*-Methyl-2-Pyrrolidone as a Solvent for Poly(Vinyl Alcohol)**

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## **Synopsis**

NMP (*N*-methyl-2-pyrrolidone) and its mixtures with water have been investigated as solvents for PVA [poly(vinyl alcohol)]. Judging from the higher exponent in the Mark-Houwink equation, NMP appears to be a better solvent than water. The equation found is

$$[\eta] = 1.69 \times 10^{-4}(M_v)^{0.79}$$

for solutions in NMP at 30°C. Although the viscosity of NMP-water mixtures goes through a maximum when the molar ratio of NMP to water is 1:2, the intrinsic viscosity for PVA exhibits neither a maximum nor a minimum in mixtures ranging from pure water to pure NMP. As in aqueous solutions, the intrinsic viscosity in NMP solutions decreases slightly with increasing temperatures from 20 to 50°C.

## **INTRODUCTION**

Except for dimethylsulfoxide (DMSO), all solvents for poly(vinyl alcohol) (PVA) which are well-documented contain water.<sup>1</sup> In most applications, as in most studies, water is the sole solvent. Since an application of some interest for the polymer is its reaction to form water-insoluble derivatives, the investigation of *N*-methyl-2-pyrrolidone (NMP) as a solvent has some merit.

Pure DMSO and 15% water, by volume, in phenol are better solvents than water for PVA, as indicated by the fact that intrinsic viscosity is proportional to a higher power of the molecular weight. The reported values for the exponent are 0.84 for DMSO<sup>2</sup> and 0.775 for 15% water/phenol,<sup>3</sup> compared to 0.62–0.64 for water.<sup>4</sup> On the other hand, mixtures of water and DMSO are relatively poor solvents for PVA. A similar lowering of intrinsic viscosity is observed for PVA in mixtures of more than 80% by volume of dimethylformamide in water. When some nonsolvents (acetone, dioxane, formic acid, formaldehyde, and 1-propanol) are added to aqueous solutions, the intrinsic viscosity goes through a maximum.<sup>5,6</sup> The maximum occurs for about 25% of nonsolvent in water. Some other nonsolvents (methanol and ethanol) reduce intrinsic viscosity.

NMP is a typical dipolar aprotic solvent. Because of the doubly bound oxygen, it is a strong electron donor or, in other words, a good hydrogen acceptor. Its high polarity, as reflected in the high boiling point (202°C) and high dipole

moment (4.09D) can be attributed to the partial double bond character of its carbonyl carbon-nitrogen bond.<sup>7</sup>

Scheme I. Major Resonance Forms of NMP



NMP is widely employed as a chemical reaction medium, as a polymer solvent, and as a selective solvent for petrochemical and industrial fluids and gases.<sup>8</sup>

Like other aprotic solvents such as dimethyl formamide and DMSO, NMP is highly associated in the liquid state. The associated structures of varying size are formed through the tertiary amide group in NMP. These associates exist at room temperatures but break down at higher temperatures. This association behavior is similar to that exhibited by DMSO.<sup>9</sup>

### EXPERIMENTAL PROCEDURES

Ordinary Ubbelohde viscometers were used for the measurement of viscosities at temperatures 20–50°C. The NMP (Eastman Kodak, practical grade) was distilled before use. The PVA samples are listed in Table I.

At concentrations below 0.5 g/dl, conventional plots according to the Huggins and Kraemer equations<sup>10</sup> were found to be adequate for the estimation of intrinsic viscosity. Under some circumstances, the Martin equation was used also<sup>10</sup>:

$$\text{Huggins: } (\eta_{sp}/c) = [\eta] + k'[\eta]^2c \quad (1)$$

$$\text{Kraemer: } (\ln\eta_r)/c = [\eta] - k''[\eta]^2c \quad (2)$$

$$\text{Martin: } \log(\eta_{sp}/c) = \log[\eta] + K''[\eta]c \quad (3)$$

Here  $c$  is concentration (g/dl),  $\eta_r$  is relative viscosity,  $\eta_{sp}$  is specific viscosity ( $\eta_r - 1$ ), and  $[\eta]$  is intrinsic viscosity (dl/g). Following the recommendation of Pritchard,<sup>4,11</sup> the equation used to relate intrinsic viscosity in water at 30°C to the viscosity-average molecular weight  $M_v$  is

$$[\eta] = 4.53 \times 10^{-4}(M_v)^{0.64} \quad (4)$$

PVA was dissolved in water by heating the ingredients together to about 95°C

TABLE I  
Poly(Vinyl Alcohol) Samples Used in Study

	Sample No.			
	I	II	III	IV
Intrinsic viscosity (water dl/g, 30°C)	1.23	1.03	0.41	0.87
$M_v$ ( $\times 10^{-4}$ ) <sup>a</sup>	23.2	17.6	4.2	—
Designation <sup>b</sup>	Lemol 75-98	Vinol 165	Elvanol 70-05	Elvanol 50-42
% Hydrolysis <sup>b</sup>	98	99.7+	98.5–100	86–89
Comments <sup>b</sup>	—	“Superhydrolyzed”	—	—
Supplier	Bordon Co.	Air Products and Chemicals	DuPont	—

<sup>a</sup> From eq. (4).

<sup>b</sup> Manufacturer's data.

and in NMP to about 110°C. All other solutions were made by dilution of master solutions by appropriate solvents.

## RESULTS AND DISCUSSION

### N-Methyl-2-Pyrrolidone Solutions

No gelling was observed for solutions of PVA (sample II) in NMP or water at concentrations of less than 1 g/dl over periods of several days. In fact, there was no detectable change in viscosity over a carefully monitored 24-hr period. On the other hand, solutions of 5% PVA (I and II) in NMP usually gelled within a few hours of cooling to 30°C.

Both the Huggins constant  $k'$  and the intrinsic viscosity can be used as criteria of solvent "goodness." A low value of  $k'$  (less than 0.4) is often associated with a good solvent, although it is a less reliable indicator than a high value of intrinsic viscosity.

The Huggins constant  $k'$  of about 0.45 in water is high enough to indicate the poor solvating ability of water (Table II). The effect of temperature on the Huggins slope constant is not very noticeable. The low value of  $k'$ , about 0.2, indicates that NMP is a comparatively good solvent for PVA. In general, the higher the intrinsic viscosity, the more expanded the polymer chain in solution, and thus the better the solvent. A comparison of the intrinsic viscosities in NMP and water shows that NMP is a better solvent.

Theoretically, the intrinsic viscosity can be related to molecular weight  $M$ , and the expansion factor  $\alpha$ , by the following equation<sup>12</sup>:

$$[\eta] = KM^{1/2}\alpha^3 \quad (5)$$

where

$$K = \Phi (\overline{r_0^2}/M)^{3/2} \quad (6)$$

Since the root-mean-square end-to-end distance,  $(\overline{r_0^2})^{1/2}$  is dependent on the rotation of the polymer segments, it decreases with increasing temperatures. Hence  $K$  decreases with increase in temperature. The universal constant  $\Phi$  is independent of temperature.

The expansion factor  $\alpha$  depends on the heat of dilution and on the temperature. For a good solvent the heat of dilution is negative, and so  $\alpha$  decreases with temperature, while for a poor solvent, the heat of dilution is positive, and  $\alpha$  increases with temperature.

Thus the overall effect of temperature on intrinsic viscosity is dependent on the type of solvent. The decrease in intrinsic viscosity with increasing tem-

TABLE II  
Intrinsic Viscosity (dl/g) of PVA (Sample II) in Water and NMP

$T$ (°C)	Water		NMP	
	$[\eta]$	$k'$	$[\eta]$	$k'$
20	1.10	0.47	2.56	0.20
30	1.03	0.45	2.50	0.18
50	0.93	0.46	2.27	0.20

perature for PVA in NMP and in water is shown in Table II. Using the intrinsic viscosity at 20°C as a reference value, the following equations express the relation between  $[\eta]$  and  $T$  (°C):

$$[\eta]_{T^{\circ}\text{C}} = [\eta]_{20^{\circ}\text{C}}(1.059)^{-(T-20)/10} \text{ PVA in water} \quad (7)$$

$$[\eta]_{T^{\circ}\text{C}} = [\eta]_{20^{\circ}\text{C}}(1.043)^{-(T-20)/10} \text{ PVA in NMP} \quad (8)$$

To obtain the parameters in the Mark-Houwink equation, relating intrinsic viscosity and viscosity-average molecular weight, all three PVA samples (I–III) were used. The results are shown in Figure 1.

Knowing the intrinsic viscosities in water, the molecular weights of the three samples were calculated using eq. (4). The straight line of Figure 1 yields the following equation for PVA in NMP at 30°C:

$$[\eta] = 1.69 \times 10^{-4} [M_v]^{0.79} \quad (9)$$

Since only three polydisperse samples were available, rigorous values of the parameters in the equation might differ slightly from those obtained here. However, the higher exponent in the Mark-Houwink equation is a good indication that NMP is a better solvent for PVA than water. As indicated earlier, NMP is a strong proton acceptor. It is also a polar solvent. When PVA is dissolved in NMP, the hydroxyl groups of PVA form hydrogen bonds with the strong proton-accepting double-bond oxygen. The heat of formation of hydrogen bonds between the hydroxyl groups of PVA is estimated to be the same as that for water molecules.<sup>13</sup> Thus the energy of a single PVA–solvent bond can be approximately taken to be equal to the energy of water–solvent bond. The effective water–water hydrogen-bond energy in pure water is about 4.4 kcal/mol.<sup>14</sup> Holmes has estimated the water–DMSO hydrogen-bond energy to be about 4.6 kcal/mol.<sup>15</sup> The heat of solution data, of a solute in water, indicates that NMP is more “basic,” i.e., a stronger proton acceptor or electron donor, than DMSO.<sup>16</sup> Thus the water–NMP hydrogen-bond energy can be expected to be greater than the energy of a water–DMSO bond. From all this it can be inferred that the NMP–PVA hydrogen-bond energy is greater than the PVA–PVA bond energy. In a PVA–NMP system the proton-donor-acceptor type of solute–solvent interaction is much stronger and favorable than the hydrogen-bonding interaction between the hydroxyl groups of PVA. This makes NMP a better solvent for PVA than water.

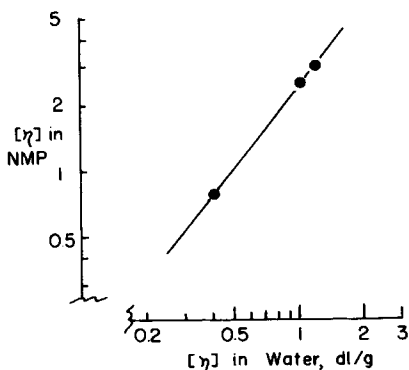


Fig. 1. Intrinsic viscosity in NMP is related to that in water by  $[\eta]_{\text{NMP}} = 2.37 ([\eta]_{\text{H}_2\text{O}})^{1.24}$ .

The exponent in the Mark-Houwink equation for PVA in DMSO is greater than that for PVA in NMP, and so as compared to NMP, DMSO is a better solvent for PVA, even though NMP is more "basic" than DMSO. One possible explanation for this is the presence of two "inert" methyl groups on DMSO in contrast to one on NMP. The steric hindrance is more pronounced in DMSO and hence the interaction between PVA molecules is less in DMSO.

This speculation is based on the assumption that hydrogen bonding plays the principal role in the interaction of the components. The effect of structural behavior such as polar-polar interaction due to suitable alignment of the PVA chains has not been taken into account.

### NMP-Water Mixtures

The addition of water to NMP results in the breakdown of the individual liquid structures<sup>16</sup> and formation of amide-water hydrogen bonds. When two liquids are mixed, bonds are broken endothermically and new ones are formed exothermically. Hence the evolution of heat when NMP and water are mixed implies that the amide-water bonds are stronger and are preferred over the water-water hydrogen bonds and amide-amide bonds.

The viscosities of NMP-water mixtures are shown in Figure 2. The viscosity has a maximum when the mole fraction of water is about 0.7. Virtanen and Korpela<sup>17</sup> have studied this system in detail. The greatest deviation from ideality occurs when the molar ratio of the amide to water is about 1:2. According to Geddes,<sup>18</sup> the abscissa of the point where the maximum deviation from ideality occurs gives the composition of any complex formed by the components, and the extreme values of the ordinate possess no real significance. Thus Virtanen and Korpela concluded that mixing NMP with water results in the formation of a

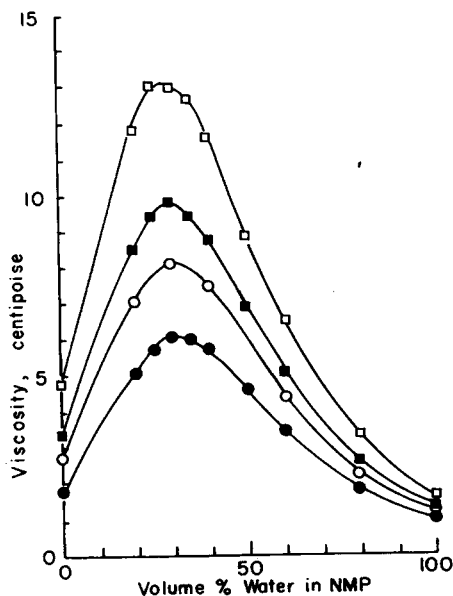


Fig. 2. Viscosity of PVA II in solvent mixtures at 20°C with concentrations (in g/dl) of 0 (●), 0.180 (○), 0.291 (■), and 0.494 (□).

TABLE III  
Intrinsic Viscosity (dl/g) and Martin Slope in Water-NMP Mixtures

Vol % water	Sample No.											
	I (30°C)		II (20°C)		II (30°C)		II (50°C)		III (30°C)		$K''$	$K''$
	$[\eta]$	$K''$	$[\eta]$	$K''$	$[\eta]$	$K''$	$[\eta]$	$K''$	$[\eta]$	$K''$		
0	2.97	0.066	2.56	0.081	2.50	0.070	2.27	0.075	0.77	0.049		
20	2.00	0.15	2.01	0.13	1.87	0.15	1.73	0.14	0.66	0.14		
30	1.82	0.14	1.76	0.14	1.68	0.15	1.59	0.15	—	—		
40	1.68	0.15	1.58	0.15	1.55	0.17	1.43	0.17	0.55	0.17		
60	1.55	0.13	1.34	0.18	1.33	0.20	1.26	0.19	—	—		
80	1.38	0.13	1.22	0.20	1.12	0.22	1.08	0.23	0.45	0.16		
100	1.23	0.15	1.10	0.18	1.03	0.18	0.93	0.18	0.41	0.10		

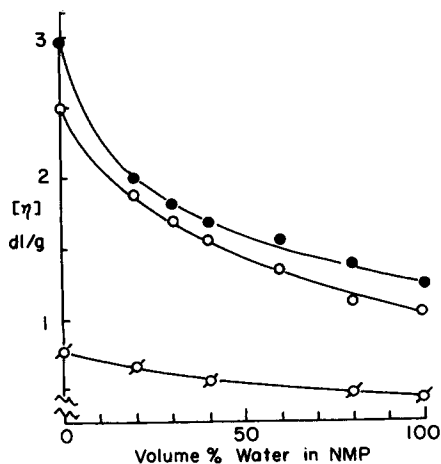


Fig. 3. Intrinsic viscosity in solvent mixtures at 30°C for PVA I (●), II (○), and III (◐).

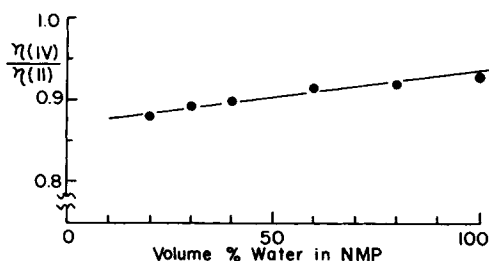


Fig. 4. Ratio of viscosities at  $c = 0.5$  g/dl for partly acetylated PVA IV and highly hydrolyzed PVA II (at 30°C).

compound which consists of one molecule of NMP associated with two molecules of water. This compound formation (of water-NMP) has been verified by Assarsson in his study on the freezing-point depressions of water-NMP mixtures.<sup>19</sup>

The intrinsic viscosities for the PVA solutions in NMP-water mixtures were obtained by extrapolating the Martin equation [eq. (3)] to zero concentration. The intrinsic viscosity decreases with increasing water concentration (Table III, Fig. 3). The addition of water reduces the number of strong proton-accepting sites, available for hydrogen bonding with the hydroxyl groups of PVA, by the formation of a 1:2 amide-water complex. This reduction in sites is reflected in the decrease in intrinsic viscosity. The "O-H" site on the water molecule can be called a "weak-site" as compared to the "doubly bound oxygen" on the NMP, which is a "strong-site." The addition of water to an NMP-PVA system results in the rapid consumption of the strong sites by H<sub>2</sub>O molecules and thus a rapid decrease in intrinsic viscosity. However, the disappearance of one "strong-site," is accompanied by the appearance of two "weak-sites," and so as more water is added, the number of "weak-sites" increase more than the decrease in "strong-sites"; thus the intrinsic viscosity drops less rapidly, until it eventually levels to that of PVA in pure water.

The Martin slope constant  $K''$  does not show any consistent trend with decreasing solvent power (Table III). This is not very uncommon, particularly

for polar polymers.<sup>20</sup> For nonpolar polymers,  $K''$  decreases with increasing solvent power. Similarly, no conclusions can be made on the dependence of  $K''$  on either temperature or molecular weight. This erratic behavior of  $K''$  can partly be due to the uncertainty involved in measuring slopes.

The presence of residual acetate groups in PVA is expected to lower the intrinsic viscosity in water. The acetate groups are "hydrophobic" and reduce the amount of solute-solvent interaction. As a result, PVA molecules are more tightly coiled. A similar lowering of specific viscosity is observed when PVA with high residual content is dissolved in NMP-water mixtures. In fact, the ratio of viscosities for two polymers (II and IV) shows that while NMP is a better solvent than water for both, the advantage is less apparent for the partly acetylated material (Fig. 4).

### CONCLUSIONS

1. NMP is a better solvent for PVA than water. This property is reflected in the values of the parameters of the Mark-Houwink equation for the two solvents.

2. The viscosity of NMP-water mixtures, and of PVA in NMP-water mixtures, goes through a maximum when the volume fraction of water in NMP is about 0.3, which corresponds to a mole fraction of about 0.7. This corresponds to the formation of an amide-water complex, which is made up of two molecules of water hydrogen-bonded with one molecule of NMP.

3. The intrinsic viscosity of PVA in NMP-water mixtures decreases with increasing amounts of water. Thus NMP-water mixtures are better solvents for PVA than pure water. The presence of some residual acetate groups in PVA does not change the above behavior.

4. The intrinsic viscosities of PVA in NMP and in water decrease with increasing temperature. The same is true for PVA in NMP-water mixtures.

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