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A spectroscopic study of the solvation of 1-vinyl-2-pyrrolidone and poly(1-vinyl-2-pyrrolidone) in different solvents

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Abstract

The solvation of 1-vinyl-2-pyrrolidone and poly(1-vinyl-2-pyrrolidone) in solvents of varying polarity, specifically water, ethylene glycol, chloroform and carbon tetrachloride, was investigated by means of Fourier transform infrared (FT-IR), FT-Raman, UV, ^{1}H and ^{13}C NMR spectroscopy. The IR and Raman measurements made it possible to establish the structures of the solvated molecules and the type of the hydrogen bonding that was obtained. From the UV results, the strength of the vinyl double bond was estimated in the different solvents. The ^{1}H and ^{13}C NMR spectra indicated that polar solvents interact with the solutes at the carbonyl group of the pyrrolidone ring, whereas nonpolar solvents interact mainly with the vinyl group in the 1-vinyl-2-pyrrolidone and with the polymer chain in poly(1-vinyl-2-pyrrolidone). © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(1-vinyl-2-pyrrolidone); Solvation; Spectroscopy

1. Introduction

In wet aluminium electrolytic capacitors, the anode is an oxidised etched aluminium foil with a rough surface, which is separated from the cathodic aluminium foil by paper, impregnated with an electrolyte. The dielectric is the oxide layer and the active cathode is the cathodic foil in combination with the electrolyte in contact with the outer surface of the oxide layer. The aluminium oxide is γ-alumina, containing active surface hydroxyl (≡ALOH) groups, which are able to react with certain electrolyte components. This can result in either adsorption or catalysis of different reactions in the electrolyte [1].

A capacitor designed for high voltage applications (>400 V) contains an electrolyte consisting of an organic solvent, e.g. ethylene glycol (EG), together with inorganic or organic solutes like dicarboxylic acids, amines as well as some additives to achieve enhanced performance. The additives are important to protect and stabilise the oxide layer, and to improve the electrical parameters as well as the non-inflammability.

One of the currently used additives in electrolytic capacitors is poly(1-vinyl-2-pyrrolidone) (PVP) which has several positive effects. It increases the working voltage of the capacitor without increasing the ESR (equivalent serial resistance) and it is not hazardous to the environment or humans. A disadvantage is, however, that it makes the electrolyte more viscous and therefore more difficult to handle in the production process.

This study forms a part of a larger research program, financed by the Swedish Research Council for Engineering Sciences and Evox Rifa AB, in order to investigate the chemistry of electrolytic capacitors with special reference to processes occurring at the interfaces between different phases. The overall intention is to increase our knowledge about the different ingredients in the electrolyte and their behaviour in the capacitor. We are also interested in the chemical processes that occur during the lifetime of the capacitor and where these processes take place. In order to understand the role of PVP in the capacitor, it is first necessary to investigate the interactions with different solvents, before studying adsorption on the oxide layer of the aluminium foil.

Solvents were chosen according to the fact that the electrolytes designed for high voltage applications mainly contain EG as a solvent with a small amount of water. In order to compare the results, we have chosen to study both polar and nonpolar solvents. Besides EG and water, we have studied carbon tetrachloride and chloroform, the later allowing higher concentrations of dissolved PVP to be achieved.

PVP is also a widely used substance in fields other than the capacitor industry, e.g. in the pharmaceutical industry, due to its nontoxicity and good complexing properties for

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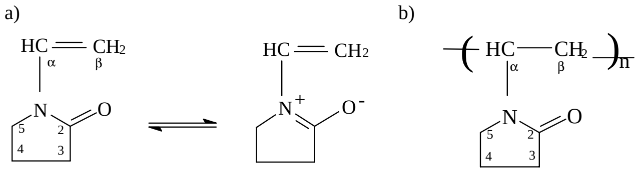


Fig. 1. (a) VP and (b) PVP.

ionic or π-electron system containing substances, such as acids or aromatic compounds [2]. The complexation of these substances can be studied by means of techniques like nuclear magnetic resonance (NMR) [3], infrared (IR) [4], Raman and UV spectroscopy [5].

2. Experimental

1-Vinyl-2-pyrrolidone (VP) (Merck 8.08518) and poly(1-vinyl-2-pyrrolidone)-K17, K30, K90 (representing different alkyl chain lengths, the larger the number the longer the chain) (PVP) (BASF) and K15 (ISP), see Fig. 1, were dissolved in solvents with different polarities to yield 10% (w/w) solutions. Ethylene glycol (EG) (Merck 1.09621), water (deionised water and heavy water), carbon tetrachloride (CCl_4) (BDH 1846) or chloroform ($CHCl_3$) (Merck 1.024445) were used as solvents. Their physical properties can be found in Table 1 [6].

IR and Raman spectroscopy can be used to study solvation, but in solutions, the solvent absorption spectrum may overlap that of the investigated substance, especially in the case of EG and water solutions where the solvents show very broad bands in the same spectral region as the solute.

Fourier transform-infrared (FT-IR) and FT-Raman spectra were acquired for all solutions and for the raw materials. The IR spectra were recorded using a Perkin–Elmer 2000 FT-IR spectrometer. PVP powder samples were analysed by diffuse-reflectance using a Perkin–Elmer DRIFT accessory. A sample dilution of 3% in desiccated KBr was used. The solutions were measured in the transmission mode using CaF_2 windows.

Raman spectra were obtained using a Perkin–Elmer 1760X FT-IR spectrometer equipped with a NIR-Raman bench, which utilises a Nd:YAG laser operating at 1064 nm. 180° back-scattering geometry and an indium gallium arsenide detector were applied. The laser power was kept constant at 1 W and at least 50 scans were accumulated to achieve the final spectrum. Liquid samples were measured in a cuvette and solid samples were analysed without dilution.

Solid state ^{13}C NMR is a very powerful tool for investigating solid polymers, and with liquid state NMR, studies of the solvation process are also facilitated. Using NMR, it is possible to investigate all the reactions occurring in both the solid and liquid phase with the same technique. NMR spectra were collected from the EG and heavy water solutions, and the solvation process in chloroform was also studied.

Spectra were recorded using a Chemagnetics CMX 360 MHz spectrometer. The ^{13}C nucleus was monitored at 90 MHz without and with proton decoupling (Waltz sequence), whereas the ^{1}H nucleus was measured at 360 MHz. Proton coupled ^{13}C spectra were used only to assign the chemical shifts. Solid state ^{13}C NMR spectra of PVP were obtained using magic angle spinning (5000 Hz) and cross polarisation. In liquid state NMR, an internal standard (TPS) and field locking was used in the case of the aqueous solutions, but in all the other cases chloroform was used as an external standard with ^{1}H and ^{13}C chemical shifts of 7.27 and 77.23 ppm, respectively. In solid state studies, the NMR spectrometer was calibrated using adamantane as external standard with ^{13}C chemical shifts of 29.51 and 38.56 ppm.

UV spectra were acquired for VP in water, EG and chloroform, but in this case, due to the high sensitivity of the method, diluted samples were used. The UV measurements were carried out on a Perkin–Elmer Lambda 2 UV/VIS spectrometer. All samples were analysed in dual beam mode using deionised water, ethylene glycol or chloroform as reference.

The IR, Raman and UV spectra were evaluated using the Spectrum Lite program from Perkin–Elmer, and the NMR spectra were evaluated using Spinsight software.

3. Results and discussion

Comparing the IR and Raman spectra of PVP with different alkyl chain lengths (K17, K30, K90), the Raman spectra seemed identical and there were only some minor differences in the IR spectra in the region of 3600–3300 cm^{-1}. A band around 3354 cm^{-1}, which is only a shoulder in the case of PVP-K17, was obtained as a more resolved peak at 3345 cm^{-1} in the longer alkyl chain substituted PVP. Differences in the IR spectra can be explained by residual amounts of buffer substances used to maintain the pH during the polymerisation.

In most of the experiments involving PVP, only PVP-K15

Table 1
Physical properties of the solvents used in the experiment [7]

	CCl4	Chloroform	EG	Water
Dielectric constant	2.238 (20°C)	4.806 (20°C)	37.7 (25°C)	80.2 (20°C)
Dipole moment	0 (25°C)	1.15 (25°C)	2.28 (20°C)	

Table 2
The carbonyl group stretching wavenumbers of VP and PVP as a function of the solvent

	C=O stretching cm^{-1}		C=C stretching cm^{-1}	
	IR	Raman	IR	Raman
PVP in	1674	1670	–	–
Water	ca 1650	1646	–	–
Ethylene glycol	1661	1659	–	–
Chloroform	1674	1670	–	–
Carbon tetrachloride	–	–	–	–
VP in	1706	1694	1629	1629
Water	1665	no	1632	1635 +shoulder
Ethylene glycol	1681	1680	1632	1633
Chloroform	1695	1693	1631	1632
Carbon tetrachloride	1712	1708	1629	1630

was used, because of its higher solubility in the different solvents. PVP-K15 has an identical IR spectrum to PVP-K17, even though they were produced by different manufacturers.

The pure liquid VP has two very strong vibration bands in the IR spectrum. The first is at 1629 cm^{-1}, which is a carbon double bond stretching vibration, corresponding to olefinic C=C stretching which is usually found in the region of 1680–1630 cm^{-1}. The second is at 1706 cm^{-1}, which is due to the carbonyl stretching, as lactams in five-membered rings have C=O stretching between 1750 and 1700 cm^{-1} [7]. In the present case, both frequencies appear in the lower region because the olefinic group is monosubstituted and there is a possibility for conjugation with the nonbonding electron pair of the nitrogen and the carbonyl group. Owing to the overlapping electron orbitals, a resonance system involving five atoms can be formed, which weakens both C=C and C=O force constants, thus lowering the frequencies.

In the case of PVP, a broad C=O stretching band can be found at 1675 cm^{-1}. As PVP contains no C=C double bond as found in VP, there is no possibility of forming the same resonance system involving five atoms, but the nonbonding electron pair on the nitrogen can still lower the frequency. In addition, the carbonyl group in PVP can form intramolecular hydrogen bonds, which are stronger in the solid phase than in the liquid. The band is broad due to the many different conformations of the monomer units in the polymer molecule, where the carbonyl groups can be differently oriented.

In the corresponding Raman frequencies of VP, the carbonyl stretching vibration appeared at 1694 cm^{-1} and the carbon double bond at 1629 cm^{-1}; in the case of the polymer the carbonyl frequency was found at 1670 cm^{-1}. After the dissolution of PVP and VP in the different solvents, FT-IR and FT-Raman spectra were recorded.

The characteristic frequencies are shifted in the different solvents. It is difficult to determine the frequencies of VP and PVP directly in solutions, since the solvents have broad absorption bands in the interesting IR and Raman regions. Therefore, spectra of the solvents were also recorded and, after normalisation, they were subtracted from the solution spectra. With $CHCl_3$ and CCl_4, this procedure was done only for the Raman spectra, as these solvents have symmetrical structures and exhibit either only a few weak bands or none at all in the IR spectral region from 4000 to 900 cm^{-1}.

In the presence of polar and protic solvents, like EG or water, the C=O and C=C frequencies are effected by the hydrogen bonding between the carbonyl group and the solvent molecules. The carbonyl and the carbon–carbon double bond stretching frequencies in the different solvents are summarised in Table 2 and the IR spectra are shown in Figs. 2 (VP) and 3 (PVP). The Raman spectra are presented in Fig. 4a (VP) and 4b (PVP).

In EG, the IR absorbance of the carbonyl group of VP appears at 1681 cm^{-1} and the C=C stretching frequency is shifted to 1632 cm^{-1}. In water, the wavenumber of the carbonyl vibration is lowered to 1665 cm^{-1}. As can be seen from the changes, mainly the carbonyl group is effected by the hydrogen bonding, which results because of a tendency to lower the force constant and the frequency. In chloroform, the shifts are smaller, the carbonyl vibration is observed at 1695 cm^{-1} and the C=C stretching occurs at 1631 cm^{-1}. In CCl_4, the carbon double bond stretching was unaffected and the carbonyl frequency increased a little compared to the pure VP, from 1706 to 1712 cm^{-1}. In the case of VP in aqueous solution, not only can the frequency shift be seen but even the ratio between the intensities of the carbonyl peak and the carbon double bond has changed as well. In all the other cases, the intensity of the carbonyl stretching band is higher than the C=C stretching, except in water. This means that, in water, the C=O stretching vibration has a decreased intensity and at the same time the position of the band shifts very much to a lower wavenumber (1665 cm^{-1}), becoming broader and exhibiting a shoulder at 1650 cm^{-1} (Fig. 2).

Comparing the Raman spectra, the same conclusion can be drawn regarding the carbonyl stretching frequencies in different solvents (Table 2 and Fig. 4a). The more polar and protic the solvent is, the lower the frequency of the C=O stretching. The only exception is water, where this band seems to disappear and a new very broad band appears between the C=O and the C=C stretching at 1644 cm^{-1}. Looking at this region more carefully, it can be seen that between 1750 and 1600 cm^{-1}, there are not only two bands attributable to the carbonyl and the C=C double bond stretching, but actually three bands in all the cases, even in pure VP. The third one is only a shoulder on the high frequency flank of the C=C stretching peak, which can be resolved by processing the second derivative of the spectra (Fig. 5). In Fig. 5, it can be seen that the frequency of the new peak increases with the polarity of the solvent: in CCl_4 it appears at 1640 cm^{-1}, and in water at 1648 cm^{-1}, and the intensity in water is much greater in comparison with that of the carbon double bond than in a nonpolar aprotic solvent. We can assign this peak to the C=N double bond in the

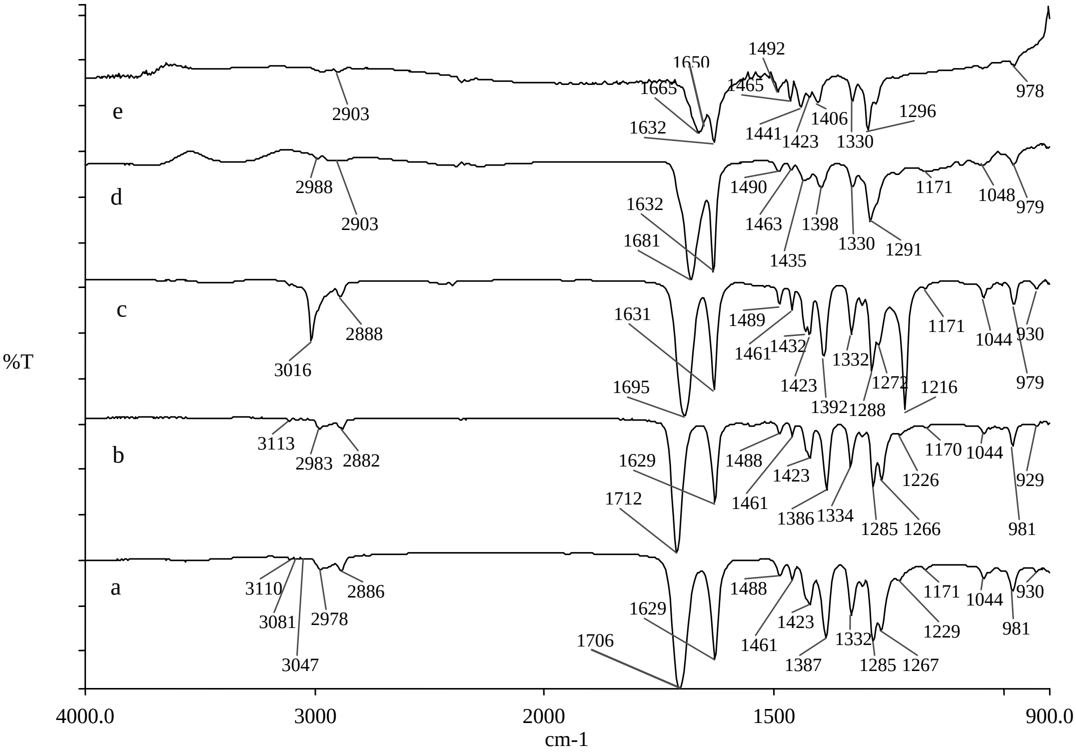


Fig. 2. FT-IR spectra of: (a) VP; (b) VP in CCl_4; (c) VP in chloroform; (d) VP in EG; (e) VP in water. In (d) and (e), the solvent contribution has been subtracted from the spectra; in (c), peaks at 1216 and 3016 cm^{-1} originate from the solvent.

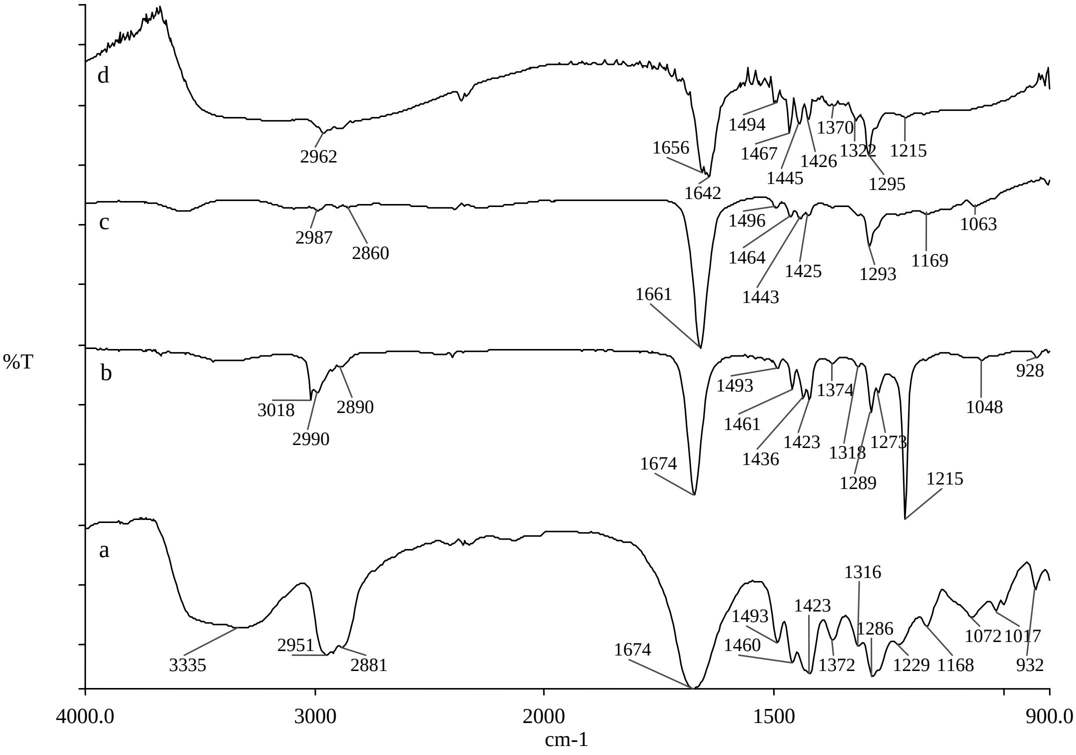
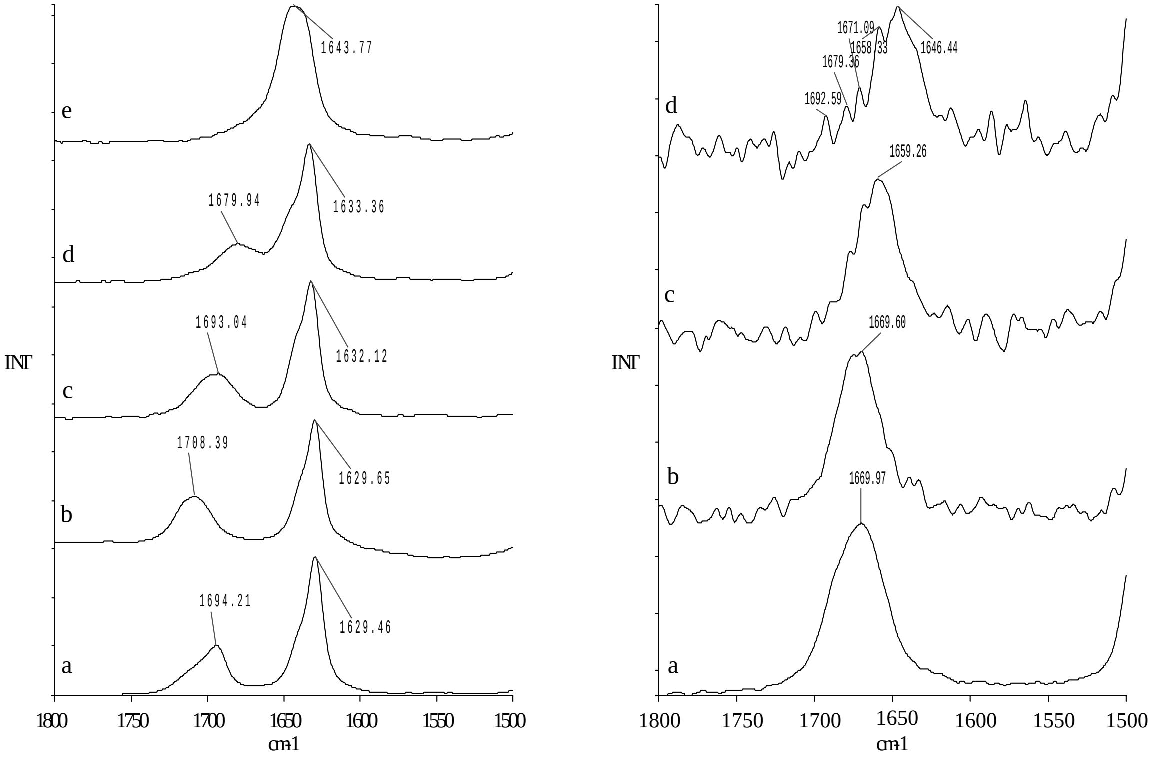


Fig. 3. FT-IR spectra of: (a) PVP; (b) PVP in chloroform; (c) PVP in EG; (d) PVP in water. In (c) and (d), the solvent contribution has been subtracted from the spectra; in (b), peaks at 1215 and 3018 cm^{-1} originate from the solvent.



(a)

(b)

Fig. 4. (a) FT-Raman spectra of: (a) VP; (b) VP in CCl_4; (c) VP in chloroform; (d) VP in EG; (e) VP in water. (b) FT-Raman spectra of: (a) PVP; (b) PVP in chloroform; (c) PVP in EG; (d) PVP in water.

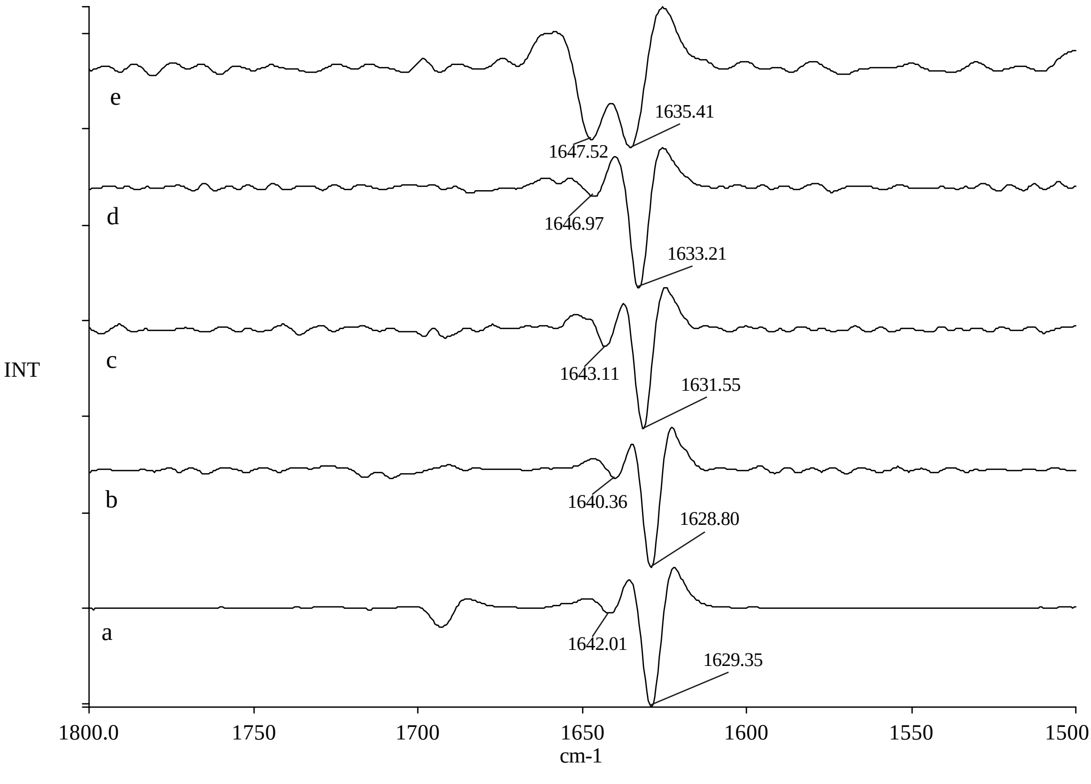


Fig. 5. Second derivatives of the RAMAN spectra of: (a) VP; (b) VP in CCl_4; (c) VP in chloroform; (d) VP in EG; (e) VP in water.

mesomeric structure of VP (Fig. 1). This peak usually appears between 1690 and 1645 cm^{-1} in –O–C=N– containing compounds [7], but conjugation lowers the frequency. When this mesomeric structure is more stabilised by the solvent, the force constant of the C=N bond increases due to the decrease in the relative electronegativity of the oxygen. The reason is hydrogen bonding. When VP is dissolved in water, the carbonyl stretching, which is originally weaker in Raman than in IR spectra, disappears from the former. Only then the C=N double bond can be seen from the mesomeric structure in combination with the C=C double bond as a broad band at 1644 cm^{-1}. This is in good correlation with the IR results, where the C=N double bond stretching was also found in aqueous solution, as the already mentioned shoulder at 1650 cm^{-1}. In the other solvents, this vibration is probably too weak to be detected by IR.

The carbonyl stretching frequencies of PVP in different solvents are lower than in the case of VP, but comparing these values to those of the solid polymer, it can be concluded that the overall changes are smaller than were observed in the case of VP (Figs. 3 and 4b). These observations can be explained by partial changes in the intramolecular hydrogen bonds, existing in the PVP, to solute–solvent intermolecular hydrogen bonds.

As mentioned before, not only is the carbonyl group effected by solvation, but in the case of VP the carbon double bond is too. This can be seen in both the IR and Raman spectra (Figs. 2 and 4a), but UV spectroscopy is particularly useful for following this effect. The vinyl group has a strong UV adsorption band around 233–240 nm, depending on the solvent. Even if the two polar solvents (water and EG) are compared, the adsorption maxima for VP are at different wavelengths (Fig. 6); in ethylene glycol at 235.5 nm and in water at 233.8 nm. The difference is small compared to the effect on the carbonyl group in IR and Raman, but still detectable and reproducible. Due to the hydrogen bond formation, the electron density between the two carbons is also changed, probably due to steric effects, and this alters both the force constant and the absorption frequency.

To determine the specific carbon or hydrogen that is effected by solvation, NMR studies were performed. The assignments for carbon chemical shifts in the different solvents are tabulated in Table 3, corresponding data for hydrogen being given in Table 4 (see also notations in Fig. 1). The solid state ^{13}C NMR spectrum of PVP and the liquid state ^{1}H NMR spectrum of PVP in water can be seen in Fig. 7.

The chemical shifts for the pure VP are almost the same, or greater for C3, C4, C5 and Cα carbons as in chloroform, showing that solvation in an apolar solvent does not withdraw the electron density around these carbons. The decrease in the shifts in chloroform compared to the pure VP can be explained by the existing intermolecular interactions between the VP molecules, which are strongly affected by solvation. Looking at the trends in the shifts in going from apolar to more polar solvents, the carbon chemical shifts increase with the polarity of the solvent, but not at

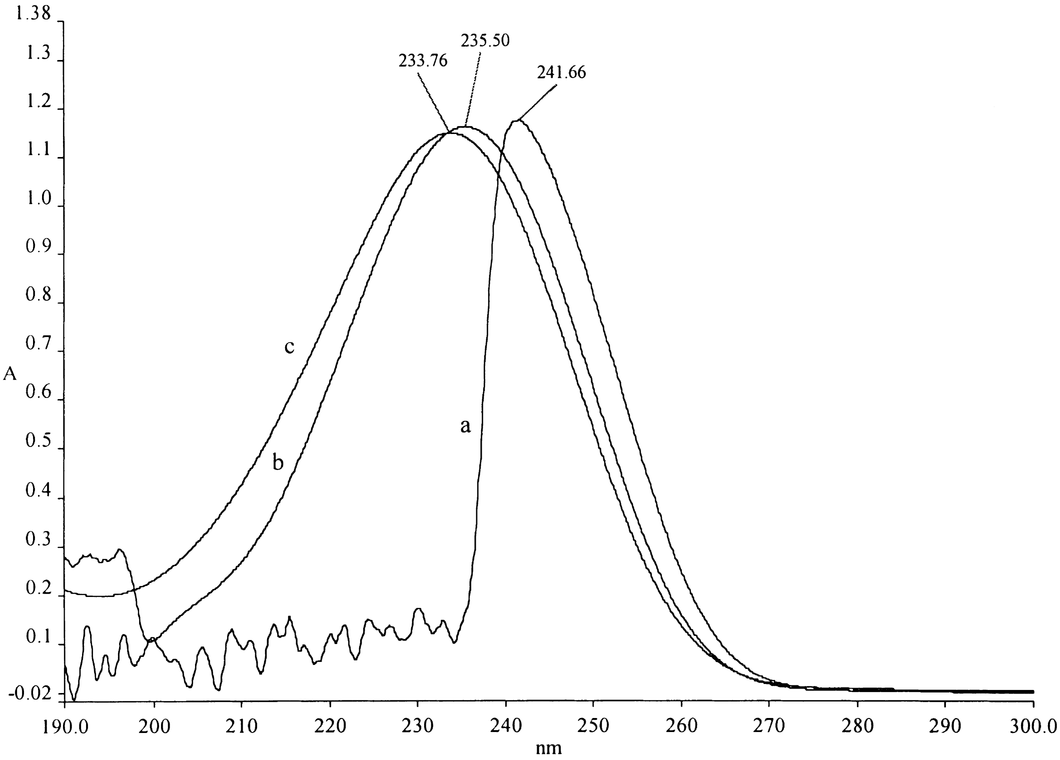


Fig. 6. UV spectra of: (a) VP in chloroform; (b) VP in ethylene glycol; (c) VP in water.

Table 3
The carbon chemical shifts in ppm of VP and PVP in different solvents

90 MHz (ppm)	VP					PVP			
	in D_2O	in EG	in $CHCl_3$	Pure liquid	SDBS [8]	in D_2O	in EG	in $CHCl_3$	Pure solid
C2	179.5	175.3	173.0	172.8	173.2	180.2	177.1	175.2	175.7
C3	34.0	31.4	30.9	31.2	31.3	34.0	31.6	31.3	32.3
C4	19.4	17.3	17.0	17.5	17.3	20.2	18.3	18.2	19.1
C5	48.1	45.2	44.2	44.6	44.5	45.6	43.7	42.5	43.5
						45.4	43.1	42.2	
						45.2	42.5	42.1	
								41.9	
Cα	131.3	129.1	128.9	129.8	129.3	48.5	45.9	45.4	50.9
						47.6	44.6	45.2	
						47.2	44.5	45.1	
								44.1	
Cβ	100.1	95.8	94.0	93.3	94.2	38.0	36.2	36.8	36.3
						37.4	35.2	35.4	
						36.5	34.3	34.7	
						35.6	33.3	33.8	
								33.2	

the same rate on every carbon. Comparing the carbon chemical shifts for VP in chloroform and in heavy water, it can be seen that the biggest deshielding effects occur at the carbonyl carbon (C2) and at the vinyl carbon (Cβ). The differences are 6.5 and 6.1 ppm, respectively, while for the other carbons, it is between 1.4 and 3.9 ppm. The other carbon atom in the vinyl group (Cα), attached to one hydrogen, remained almost unchanged and was not considerably perturbed by the solvent. Investigating the proton NMR results, the same conclusion can be drawn, the difference is greatest for the two hydrogens on the Cβ carbon and lowest for the α hydrogen. In the pyrrolidone ring, the least effected nuclei are at the C4 position.

In pure solid PVP, the assignment is more difficult, since the vinyl group is saturated and the ^{13}C chemical shifts for these carbons overlap those of the C3 and C5 carbons in the pyrrolidone ring. The situation is even more complicated in solution, because the PVP has its own conformation and the monomers are not uniformly oriented in the molecule. Therefore, an equivalent atom, in different monomer units in the chain, can have different shifts depending on the surroundings. In liquid state NMR, the line widths are

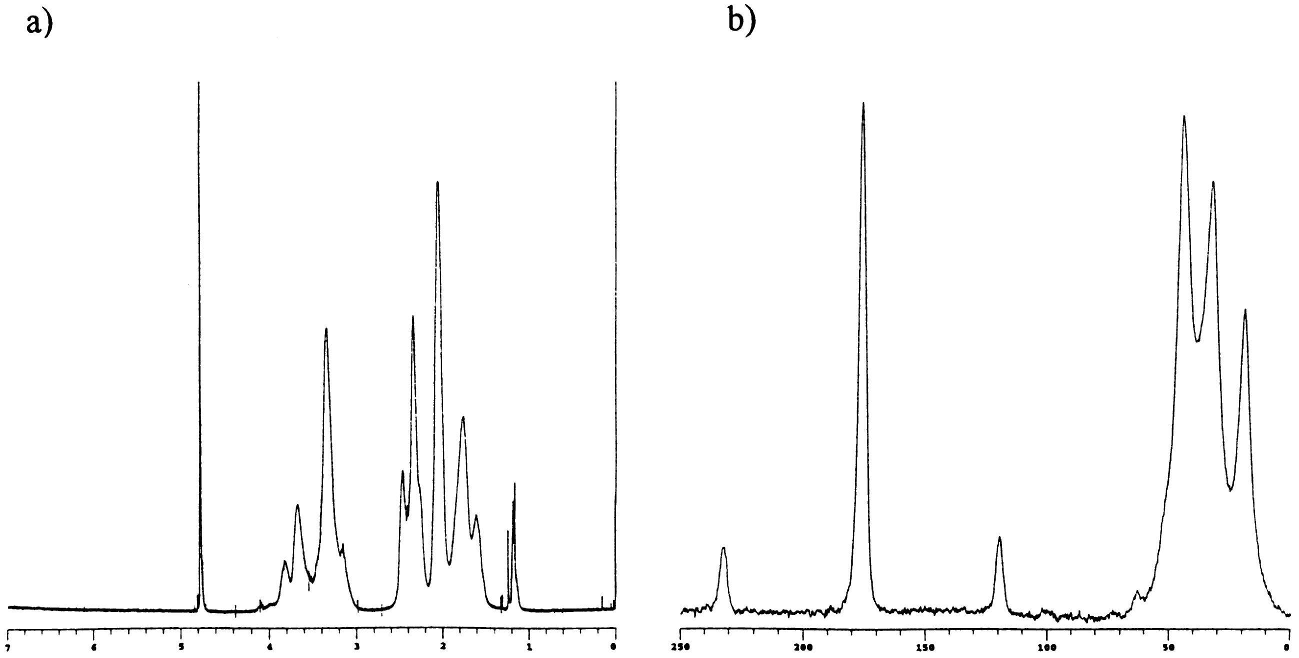


Fig. 7. (a) Liquid state ^1H NMR spectrum of PVP in water; (b) solid state ^{13}C NMR spectrum of PVP.

Table 4
The proton chemical shifts in ppm of VP and PVP in different solvents

360 MHz (ppm)	VP					PVP			
	in D_2O	in EG	in $CHCl_3$	pure liquid	SDBS [8]	in D_2O	in EG	in $CHCl_3$	solid
C3	2.55	2.61	2.35	2.59	2.49	2.46 2.41 2.33	2.42	2.26	–
C4	2.13	2.21	1.98	2.28	2.13	2.04	2.13	1.90	–
C5	3.62	under EG	3.39	3.68	3.52	3.34 3.16	3.42	3.13	–
Cα	6.95	7.09	6.93	7.23	7.09	3.82 3.68	under EG	3.76 3.46	–
Cβ	4.66	4.65	4.28	4.59	4.45 4.42	1.77x 4.42	1.85 1.60	1.59 1.47 1.32	–

narrow enough to show these splittings. In order to distinguish this type of splitting from that originating in the hydrogen–carbon coupling, proton decoupling with Waltz sequence was used to obtain simplified spectra. In the ^{13}C NMR spectra of PVP in the different solvents, three of the carbon lines split into 3–5 separate peaks representing chemically non-equivalent carbons, which belong to different conformations. The other carbon lines, even if they were not split, were much broader than in the case of VP, showing that these carbons may also experience varying environments. Comparing the chemical shifts of PVP in chloroform and in water, the same conclusion can be drawn as in the case of VP. The most affected carbon in the molecule is the one in the carbonyl group (C2). The chemical shift of the carbonyl of PVP in water is almost identical to that of VP in water, but compared to the original values (the pure chemicals), the change is smaller (4.5 ppm in the case of PVP and 6.7 ppm for VP). The solvation implies a deshielding effect on this carbon because the chemical shift of C2 increased, which results in stronger hydrogen bonds with the polar solvent than the intramolecular ones. The polar solvent mainly interacts with the PVP at the pyrrolidone ring, especially at the carbonyl group, and not at the nonpolar carbon chain.

The α carbon also exhibits large shift differences. In the case of VP in water, the peak shift increased slightly, but it was still the smallest change of all the carbons. After solving PVP, the chemical shift was not only decreased but the peak was also split into three–four lines. A decrease in the shift means that the carbon is shielded more by surrounding electrons than without solvent. This effect is greater (lower shifts) if the solvent is nonpolar.

4. Conclusion

The structures of the solvated VP and PVP molecules can be elucidated by FT-IR and FT-Raman. From the FT-IR and FT-Raman measurements, it was concluded that, in all cases there are two mesomeric structures formed by VP. In pure VP and in VP dissolved in nonpolar solvents, the carbonyl structure dominates, while in a very polar solvent, like water, the other structure is more stabilised by the solvent, implying that the C=N double bond becomes stronger and the C=O group is invisible in the Raman spectra. From the shift of the carbonyl group frequency, the strength of the hydrogen bond between the solvent and the solutant can be estimated. The carbonyl frequency shifts indicate that, in PVP, the hydrogen bonds are mainly passing from intramolecular to intermolecular bonds.

From the UV measurements the changes related to the vinyl group can be followed. This technique is limited to VP, because PVP has no sensitive UV active group. Solvation in a nonpolar solvent gives a sharper peak shifted to a higher wavelength, which implies a strengthening of the carbon–carbon double bond.

Applying ^{13}C NMR, changes in all the carbons can be followed as well as the changes in the double bond. Both the ^{13}C NMR and the ^{1}H NMR results support the conclusions drawn from the above mentioned investigations. Polar solvents interact with VP and PVP at the pyrrolidone ring, particularly the carbonyl group. Nonpolar solvents break down the existing intramolecular hydrogen bonding structure and PVP from the polymer carbon chain side, causing a slightly higher electron density between the two vinyl carbons.

In an electrolytic capacitor, polar solvents are generally preferred for dissolving the ionic ingredients and to keep the conductivity at a reasonably high level.

Referring to this study, the solvation of PVP in capacitor electrolytes is a result of an interaction on the pyrrolidone ring, leaving the nonpolar alkyl chain relatively undisturbed.

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