

STUDIES ON THE ELECTRICAL PROPERTIES OF P2VP·nI₂ COMPLEXES

HUEI-MEI TSAI and HSIEN-WEN KO

Electrochemical Department, Materials R & D Center, Chung Shan Institute of Science and Technology, Lungtan, Taiwan (Republic of China)

Summary

The electrical conductivities of iodine complexes of poly(2-vinylpyridine) (P2-VP·nI₂, n = 1 - 8) of different molecular weight P2-VP (M.W. 5 × 10⁴, 3 × 10⁵) were obtained in the temperature range -45 °C to 50 °C. An Arrhenius type exponential relationship, $\sigma = \sigma_0 \exp(-\epsilon/kT)$ was found for n = 3 - 8. The P2-VP·nI₂ complexes prepared from the lower molecular weight P2-VP (M.W. 5 × 10⁴) showed a sudden change in conductance around -10 °C, whereas no such transition was observed in the experimental temperature range for the higher molecular weight P2-VP (M.W. 3 × 10⁵). In NMR studies, no chemical shift was observed on the aromatic hydrogen positions. This indicates that bonding between nitrogen and iodine is insufficiently strong to affect the chemical environment.

Introduction

The lithium-iodine battery is a long shelf life, low drain, solid electrolyte battery with iodine complexes of poly(2-vinylpyridine) (P2-VP·nI₂) as cathode material. It has been recognized as the most reliable power source for implanted heart pace-makers. The properties of P2-VP·nI₂ complexes have attracted many investigations. In their initial report in 1967, Gutman *et al.* [1] described the cathode material as charge transfer complexes with a relatively high conductivity. The so called "charge transfer complexes" have been extensively investigated, particularly in the case of monomers such as pyridine and its derivatives [7], with the heterocyclic aromatic system behaving as electron donors. Two types of electron donation are possible: one is the Mulliken's "outer complex" (Py·I₂) which would be a molecular complex of the usual type, and the other is the "inner complex" ([PyI]⁺ I⁻) which is essentially an ionic structure. The liberated I⁻ ions may form I₃⁻ with I₂. Electron spin resonance spectroscopic studies of P2-VP·nI₂ by Mclean and Beecher [2] showed a single, narrow signal with a g-value of 2.002, indicating the presence of free electrons. Phillips and Untereker [3] measured the amount of iodine moved from one position

to another in a test cell and found that ionic conduction contributed no more than 10% of the total conduction.

Phillips and Untereker [4] also studied the phase diagram of the I_2 -P2-VP system and found a eutectic point at $X_{I_2} = 0.78$ ($n = 3$, 3 moles of iodine per mole of nitrogen in the polymer) where conductivity exhibited a maximum of $10^{-3} \Omega^{-1} \text{ cm}^{-1}$. As more iodine is added, the conductivity decreases due to the dilution effect of the iodine phase. They applied nuclear magnetic resonance spectroscopy to the study of discharged cathode material and concluded that α -hydrogen on the aliphatic part was replaced by iodine but neither the β -hydrogen nor the aromatic hydrogen atoms were replaced [5].

Experimental

Two average molecular weights, 5×10^4 (Aldrich) and 3×10^5 (Fluka), of P2-VP were used. Stoichiometric amounts of P2-VP and I_2 with $n = 1 - 8$ were mixed and heated at 120°C for 6 days in a sealed glass ampoule. The complexes were iodine-like, purple-black and very sticky. The smaller the n value, the stickier the complex, which becomes brittle and granular with $n = 1$ and 2. The sticky sample ($n = 3 - 8$) was rolled to a thickness of 0.5 mm and cut to a diameter of 16 mm while the granular sample ($n = 1 - 2$) was pressed into a pellet in a die at 340 MPa. The disk was then sandwiched between two pieces of stainless steel as electrodes, and placed in a special cell made from Teflon. The conductance was measured by an HP-4194A impedance analyzer at 1 KHz with temperatures ranging from -45°C to 50°C .

For NMR studies the complex ($P2\text{-VP} \cdot nI_2$) was pumped to remove excess free iodine, and was then dissolved in DMSO-d_6 . Part of the sample was used for the quantitative determination of iodine by the Schöniger method.

Results

Figures 1 and 2 give the conductivity curves with varying n values, for P2-VP of molecular weight 5×10^4 and 3×10^5 , respectively. These conform to the general shape of the conductivity curves generated by all the $P2\text{-VP} \cdot nI_2$ complexes studied. The reciprocals of temperatures *versus* conductivities were plotted for each of the samples at various n s, and an Arrhenius type exponential relationship, $\sigma = \sigma_0 \exp(-\epsilon/kT)$, where σ is the conductivity and ϵ is analogous to activation energy, was found for $n = 3 - 8$. Figure 3 shows a typical plot for $n = 3$. A sudden change in conductance around -10°C was found for the lower molecular weight P2-VP. For the higher molecular weight P2-VP, no such transition was observed in the temperature range studied. A compilation of the results is shown in

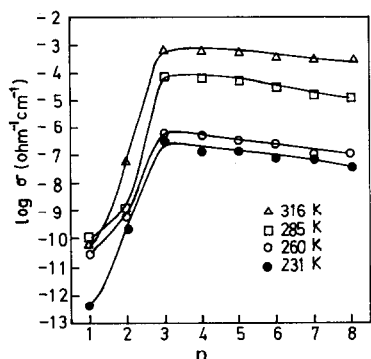


Fig. 1. The conductivity curves of P2-VP· nI_2 complexes. M.W. of P2-VP = 50 000, source: Aldrich.

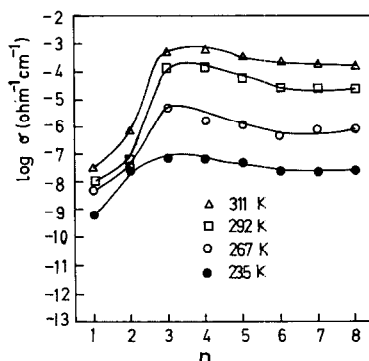


Fig. 2. The conductivity curves of P2-VP· nI_2 complexes. M.W. of P2-VP = 300 000, source: Fluka.

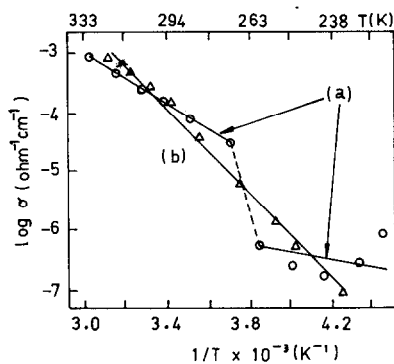


Fig. 3. Dependence of conductivity on reciprocal of temperature for P2-VP· $3I_2$ complexes (a) M.W. = 50 000; (b) M.W. = 300 000.

TABLE 1

Conductivity parameters for P2-VP· nI_2 complexes

n	M.W. = 5×10^4 *		M.W. = 3×10^5	
	σ_0 ($\Omega^{-1} \text{ cm}^{-1}$)	ϵ (eV)	σ_0 ($\Omega^{-1} \text{ cm}^{-1}$)	ϵ (eV)
3	2.95×10^3	0.43	2.87×10^8	0.73
4	6.03×10^4	0.51	1.04×10^8	0.68
5	6.03×10^3	0.46	4.79×10^8	0.75
6	1.07×10^4	0.48	6.31×10^8	0.78
7	5.37×10^2	0.42	1.23×10^9	0.79
8	1.95×10^4	0.52	1.70×10^8	0.80

*The conductivity parameters determined above transition temperature.

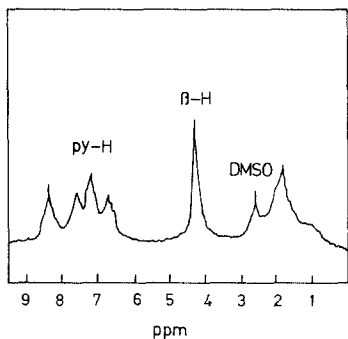


Fig. 4. NMR spectrum of $P2-VP \cdot nI_2$ (low M.W. P2-VP) after removal of excess free iodine ($DMSO-d_6$ as solvent, $80 \text{ MHz}^{-1}H$).

Table 1. For $n = 1$ and 2, the results were scattered because the complexes were so brittle that contact between the grains was poor.

Figure 4 shows the NMR spectrum for the lower M.W. sample which has four aromatic hydrogen peaks (6 - 9 ppm, δ) and one sharp peak of aliphatic β -hydrogen (3.5 - 5 ppm, δ). The missing α -hydrogen peak is replaced by iodine. No chemical shift of the aromatic hydrogen positions was observed. The iodine content was determined by the Schöniger method. After removal of the free iodine, the complex still has 1.5 mole of iodine molecule per mole of pyridine (for the $n \geq 2$ sample).

Conclusion

The $P2-VP \cdot nI_2$ complexes prepared from the lower molecular weight P2-VP sample (M.W. 5×10^4) showed a sudden change in conductance around -10°C . Gerasimov *et al.* [6] attributed this transition to the existence of at least two complex states — probably crystalline and amorphous. For the higher molecular weight sample of P2-VP, no such transition was observed in the temperature range studied. The activation energies of the lower molecular weight complexes (mean 0.47 eV) are smaller than those of the higher molecular weight complexes (mean 0.76 eV). NMR studies indicate that bonding between nitrogen and iodine is not sufficiently strong to affect the chemical environment, and there is no inner complex formation in $P2-VP \cdot nI_2$. The conductivity maximum which occurs at about 3 moles of iodine per mole of pyridine is the result of dipole interaction of the outer complex with nearby I_2 .

References

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