Electrochemical properties of complexes of iodine with cyclized poly(acrylonitrile) and 2-poly(vinylpyridine)

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(Received 2 April 1985)

Electrochemical and conductivity measurements have been performed on the iodine complexes of cyclized poly(acrylonitrile) and 2-poly(vinylpyridine). The thermodynamic activity of iodine as a function of iodine content was determined using cells of the type polymer$(I_2)_x$|AgI|Ag. The results indicate that chemical bonding between iodine and polymer is relatively weak. The conductivity data show a strong dependence of conductivity on the iodine content of the complex.

(Keywords: iodine; complexes; poly(acrylonitrile); poly(vinylpyridine); conductivity; free energies)

INTRODUCTION

2-Poly(vinylpyridine) (2-PVP) and cyclized poly(acrylonitrile) (CPAN) react with iodine to form conducting polymers[1-4]. Interest in 2-PVP–I_2 has been strong over the past decade because of its utilization as a component in electrochemical power sources for heart pacemakers. Considerably less attention has been paid to CPAN–I_2. A similar feature of the structure of CPAN and 2-PVP is that nitrogen atoms form part of an alternating system of double and single bonds (see *Figure 1*). In the case of 2-PVP, however, the alternation occurs only in the individual hexagonal rings.

Phase equilibria work has been performed on the 2-PVP–I_2 system which indicates that the phase diagram is complex[4]. Brennen and Untereker[5] have reported some iodine vapour pressure and electrochemical measurements on 2-PVP–I_2 as a function of iodine concentration. There is, nevertheless, little information available on the thermodynamic activity of iodine in the complexes. In this study, we present electrochemical data on solid-state cells of the type polymer$(I_2)_x$|AgI|Ag and electrical conductivity data on the iodinated polymers.

EXPERIMENTAL

The chemicals pyrene (Py), perylene (Pe), PAN and 2-PVP were obtained, in the highest commercial grades available, from Aldrich Chemical Co. of Milwaukee, Wisconsin. PAN was heated in a sealed, evacuated Pyrex tube for 7 days at 180°C and was subsequently heated in a pumping vacuum at 250°C for 6 h. This material we designate as CPAN-1. A portion of the CPAN-1 was further heated in a pumping vacuum at 350°C for 3 h and is designated as CPAN-2. Elemental analysis was performed on CPAN-1 and CPAN-2 samples by Schwarzkopf Microanalytical Laboratory of Woodside, New York. The compositions of CPAN-1 and CPAN-2 were found to be $C_3H_3N_{0.99}$ and $C_3H_{2.44}N_{0.90}$ respectively. I.r. spectra of CPAN-1 and CPAN-2 showed the absorption peaks corresponding to cyclized PAN[1]. The peaks for CPAN-2 were generally broader. We conclude from the data that CPAN-1 and CPAN-2 are primarily cyclized PAN. CPAN-2 has been degraded somewhat by the higher temperatures resulting in a loss of nitrogen and hydrogen.

Preliminary information on the uptake of iodine by CPAN-1, CPAN-2 and 2-PVP was obtained by enclosing samples of each in evacuated tubes with iodine at 90°C for 48 h. The polymer and iodine were in contact only through the vapour phase. The amount of iodine absorbed (moles I_2/moles repeating polymer unit), as measured by the weight increase, was 0.9–1.0 for CPAN-1, 1.0–1.1 for CPAN-2 and 2.20–2.40 for 2-PVP.

Designated compositions of Pe–I_2, Py–I_2, CPAN-1–I_2 and CPAN-2–I_2 were prepared by mixing weighed amounts of iodine and organic substance and heating in sealed, evacuated tubes for 48 h at 90°C. In the case of 2-PVP–I_2, the iodine–polymer mixtures were annealed either at 50°C for 4 days, 70°C for 3 days, 90°C for 2 days or 150°C for 1 day.

For the electrochemical measurements, a sample of powdered iodine or iodinated hydrocarbon or polymer was mixed with graphite and was pressed into a pellet using a Parr pellet press. The graphite served as an inert, electrically conducting medium. The electrochemical cells were assembled in two parts. A layer of silver iodide powder was pressed on top of a layer of silver powder. The iodinated polymer or hydrocarbon pellet was placed on top of the Ag–AgI pellet and the two pellets were compressed by springs between pieces of platinum foil attached to platinum leads. E.m.f. measurements at room temperature were made using a Keithley 602 electronic voltmeter. Readings on a sample were continued until a

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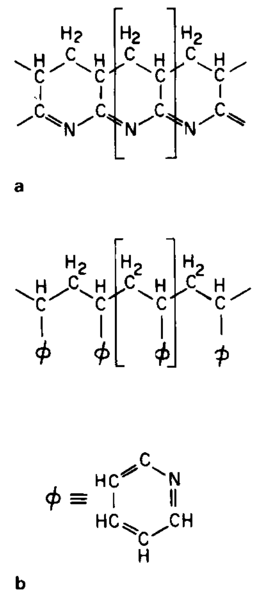

Figure 1 Structures of (a) cyclized poly(acrylonitrile) (CPAN) (b) 2-poly(vinylpyridine) (2-PVP)

steady reading (±0.5 mV) was obtained for a half-hour. Measurements with varying amounts of graphite mixed with the organic component confirmed that the voltage was independent of graphite content within wide limits. The reproducibility of voltage readings, taking into account day to day voltage changes on the same sample and variations from sample to sample of the same composition prepared separately was generally within ±10 mV.

The electrical conductivity of the iodinated polymers was measured by using a four probe van der Pauw method[6–8] on pressed pellets. Sample pellets, 13 mm in diameter and about 1 mm in thickness, were formed by compressing the material in an evacuable die with a Carver press. Pellet thickness was determined by means of a micrometer. Current to the sample was supplied by a Power Design Model 5020 constant voltage source. Output d.c. voltage was detected by a Keithley Model 191 Digital Multimeter linked to a Fluke Model 2240B Datalogger. Electrical contacts were made by using copper electrodes in earlier work and was subsequently replaced with platinum contacts. Measured sample resistance was independent of the types of contacts used and was also verified for ohmic behaviour. The electrical conductivity of the iodinated polymers was measured at room temperature.

RESULTS AND DISCUSSION

E.m.f. data were obtained on electrochemical cells of the type $I_2(c)|AgI|Ag$ at room temperature. $I_2(c)$ represents either pure I_2 or iodine complexed in varying amounts with the polycyclic hydrocarbons, Py and Pe, or with CPAN-1, CPAN-2 or 2-PVP. We assume electrochemical reversibility and the following electrode reactions

$$I_2(c) + 2e = 2I^-(AgI) \qquad (1a)$$

$$2Ag - 2e = 2Ag^+(AgI) \qquad (1b)$$

The overall cell reaction is

$$2Ag + I_2(c) = 2AgI \qquad (1)$$

On the basis of standard thermodynamic relationships it follows that

$$\bar{G}_{I_2}(c) - \bar{G}^*_{I_2} = -nF(\varepsilon^* - \varepsilon) = RT\ln(a_{I_2}/a^*_{I_2}) \qquad (2)$$

The difference of the two terms on the left is the relative partial molar free energy of iodine i.e. the difference between the partial molar free energy of iodine in the complex and in pure, solid iodine; n is the number of electrons transferred, 2; F is Faraday's Number; ε^* and ε are the *e.m.f.*'s of the cell with pure iodine and complexed iodine respectively; a_{I_2} and $a^*_{I_2}$ are the thermodynamic activities of iodine in the complex and in pure iodine, respectively.

E.m.f. data obtained on the various samples are shown in *Figures 2* and *3*. In *Figure 2*, data on CPAN-1–I_2 and 2-PVP–I_2 are compared to data on Py–I_2 and Pe–I_2. It is interesting to note that breaks in the curves for CPAN-1–I_2 and 2-PVP–I_2 occur at the approximate compositions CPAN-1$(I_2)_{1.0}$ and 2-PVP$(I_2)_{2.3}$. These compositions correspond to the maximum uptake of iodine from the vapour, noted above. One may conclude that the thermodynamic activity of iodine at these compositions approaches that of pure, solid iodine.

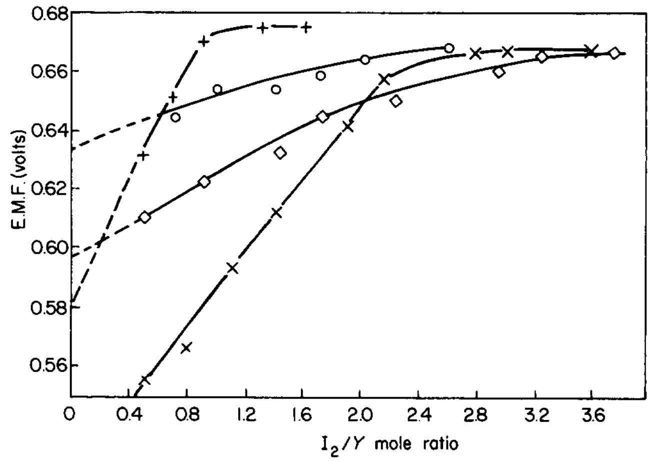

Figure 2 Variation of cell voltage with iodine content; (+), $Y \equiv$ CPAN-1 repeat unit; (×), $Y \equiv$ 2-PVP repeat unit, 90°C anneal; (○), $Y \equiv$ Py; (◇), $Y =$ Pe

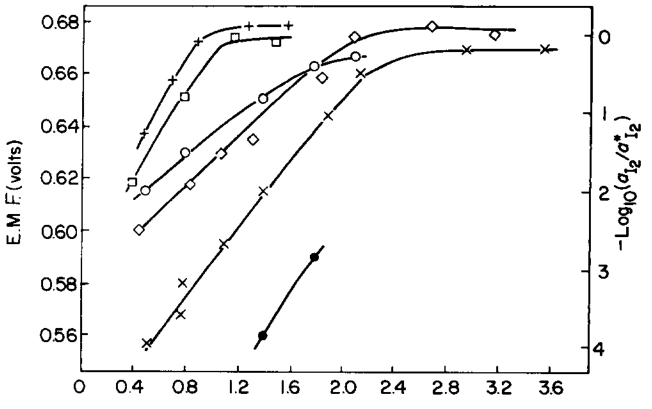

Figure 3 Variation of cell voltage with iodine content; (+), $Y \equiv$ CPAN-1 repeat unit; (□), $Y \equiv$ CPAN-2 repeat unit; (○), $Y \equiv$ 2-PVP repeat unit, 50°C anneal; (◇), $Y \equiv$ 2-PVP repeat unit, 70°C anneal; (×), $Y \equiv$ 2-PVP repeat unit, 90°C anneal; (●), $Y \equiv$ 2-PVP repeat unit, 150°C anneal

Free energies of formation of the complexes per mole of I_2, ΔG, were calculated by numerical integration of the expression[9]

$$\Delta G=\left(\frac{1-X'_{I_2}}{X'_{I_2}}\right)\int_0^{X'_{I_2}}\frac{\bar{G}_{I_2}-\bar{G}^*_{I_2}}{(1-X_{I_2})^2}\,\mathrm{d}X \qquad (3)$$

X_{I_2} is the mole fraction of iodine complexed with the organic substance; X'_{I_2} is the mole fraction of iodine at the composition where the thermodynamic activity of iodine approaches that of pure iodine. Since the integration must start at $X_{I_2}=0$, the data in *Figure 2* were extrapolated to a mole ratio of iodine to organic species of 0.

X'_{I_2} values for CPAN-1–I_2 and 2-PVP–I_2 were selected to correspond to iodine to organic species mole ratios of 1.0 and 2.3 respectively. Mole ratios of 2.0 and 2.9 were selected for Py–I_2 and Pe–I_2, respectively, because other studies[10] have shown that these ratios correspond to the maximum uptake of iodine in these systems.

Free energies of formation were calculated by applying Equation (3) to the data in *Figure 2*. The results are given in *Table 1*. Free energy values for $Py(I_2)_{2.0}$ and $Pe(I_2)_{2.9}$ calculated from iodine vapour pressure measurements[10] are listed for comparison. The values for AgI, $Py(I_2)_2$ and $Pe(I_2)_{2.9}$ obtained by the *e.m.f.* method are reasonably close to the values obtained by the other methods. This supports the validity of the *e.m.f.* method used here. The free energies of formation of all the complexes are relatively low indicating that the bonding between iodine and the organic species is weak.

E.m.f. data for different samples of CPAN–I_2 and 2-PVP–I_2 are shown in *Figure 3*. The data on CPAN-1 and CPAN-2 are very similar. In the case of 2-PVP–I_2, increasing the annealing temperature results in a decrease in iodine activity. Samples annealed at a temperature of 150°C could not be measured above a mole ratio of 1.8 because the material was too viscous to use. The *e.m.f.* values for 2-PVP–I_2 samples annealed at 50°C, 70°C and 90°C approach that of pure iodine at a mole ratio of about 2.3. The *e.m.f.* data on 2-PVP–I_2 do not show correspondence to the phase diagram of Phillips and Unterker[4]. This may be attributed to the complex nature of the phase diagram and the possibility that phase changes may not be completely reversible in this temperature range.

Electrical conductivity data for CPAN–I_2 and 2-PVP–I_2 samples at room temperature are shown in *Figures 4* and *5*, respectively. It is observed that the CPAN–I_2 and 2-PVP–I_2 curves reach plateaus at mole ratios of about 1.0 and 2.3, respectively. These ratios correspond to the compositions at which the thermodynamic activities of iodine approach that of pure iodine. The implication in the case of CPAN–I_2 is that free iodine is present above a mole ratio of 1. The significance of the plateau is less clear in the case of 2-PVP–I_2 since the phase diagram is complex. Lerner measured the electrical conductivity of CPAN–I_2[1] samples in the form of fibres, rather than pressed pellets. His conductivity values are seen in *Figure 4* to be somewhat higher than ours. The conductivity values of Untereker *et al.* (*Figure 5*), obtained on 2-PVP–I_2 samples at mole ratios above 2 are in the same range as our values.

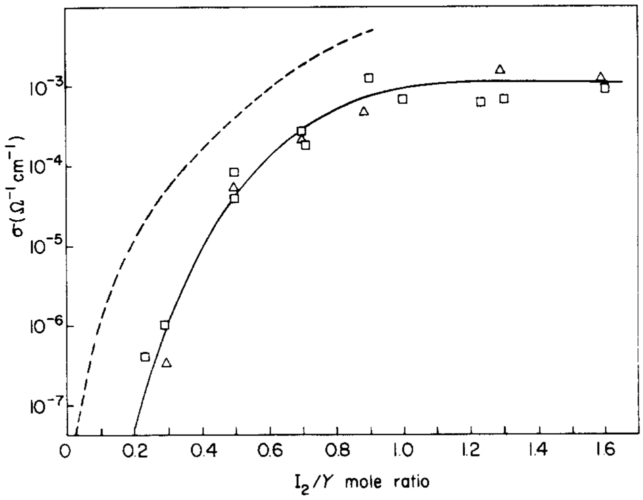

Figure 4 Variation of conductivity with iodine content; (□), $Y\equiv$ CPAN-1 repeat unit; (△), $Y\equiv$CPAN-2 repeat unit; (– – –), data of N. R. Lerner (ref. 1)

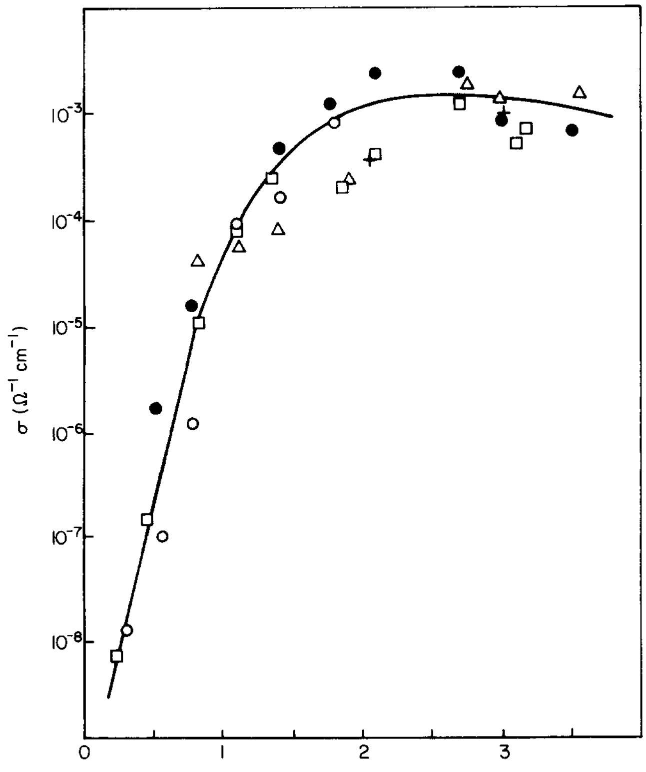

Figure 5 Variation of conductivity with iodine content; $Y\equiv$2-PVP repeat unit; (●), 50°C anneal; (□), 70°C anneal; (△), 90°C anneal; (○), 150°C anneal; (+), data of Phillips and Untereker (ref. 4)

Table 1 Comparison of free energies of formation of iodine complexes

	$-\Delta G$ (kcal/mole I_2)	
Reaction	*E.m.f.* method[a]	Other methods
$Ag+0.5I_2=AgI$	30.9	31.70[b]
$Py+2I_2=Py(I_2)_{2.0}$	0.8	0.2[c]
$Pe+2.9I_2=Py(I_2)_{2.9}$	1.5	0.9[c]
CPAN-1$+I_2=$CPAN-1$(I_2)_{1.0}$	2.0	
2-PVP$+2.3I_2=$2-PVP$(I_2)_{2.3}$	3.2	

[a] Estimated limits of error, ±1.0 kcal/mole I_2
[b] Handbook of Chemistry and Physics, 1981, p D-75
[c] From ref. 7, estimated limits of error, ±0.5 kcal/mole I_2

The nature of the CPAN–I_2 and 2-PVP–I_2 systems seem to be considerably different from polymeric systems such as polyacetylene–I_2. CPAN and 2-PVP are able to absorb significantly more iodine and attain electrical conductivities several orders of magnitude lower than polyacetylene. Unlike polyacetylene, CPAN–I_2 and 2-PVP–I_2 are stable in air for long periods of time. The electrical conduction mechanism in CPAN–I_2 and 2-PVP–I_2 may be much different from that in polyacetylene–I_2. The electronic and ionic contributions to conductivity in CPAN–I_2 and 2-PVP–I_2 are currently under investigation.

ACKNOWLEDGEMENTS

This work was supported by US Army Research Office Grant No. DAAG-83-K-0158 and in part by PSC-CUNY Research Award No. 6-63352.

The authors wish to thank F. J. Salzano, W. G. Wilhelm and P. Cerniglia of the Brookhaven Laboratory for valuable discussion and technical assistance and for making facilities available for the conductivity measurements.

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