

G. Hirankumar · S. Selvasekarapandian  
M. S. Bhuvanewari · R. Baskaran · M. Vijayakumar

## Ag<sup>+</sup> ion transport studies in a polyvinyl alcohol-based polymer electrolyte system

Received: 19 August 2003 / Accepted: 14 October 2004 / Published online: 2 September 2005  
© Springer-Verlag 2005

**Abstract** Thick films of pure polyvinyl alcohol and polyvinyl alcohol doped with silver nitrate with different compositions have been prepared by solution cast technique. The FT-IR spectrum confirms the complexation process. The conductivity of the pure polyvinyl alcohol is of the order of  $10^{-7} \text{ Sm}^{-1}$  at 90 °C, and its value increases by two orders of magnitude when doped with 20 wt% of AgNO<sub>3</sub>. The activation energy, calculated from the Arrhenius plot for all compositions of the poly vinyl alcohol doped with silver nitrate, is between 0.24 and 0.35 eV. The migration energy for the ion in polymer electrolyte has been calculated from the modulus spectrum, and is in good agreement with the activation energy calculated from the Arrhenius plot. The modulus spectra indicate the non-Debye nature of the material.

**Keywords** Polyvinyl alcohol · Modulus analysis · Transport properties · Polymer electrolytes · Ionic conductivity

### Introduction

Ion conducting polymers have received considerable attention as an electrolyte materials due to their technological implications in the development of solid polymer electrolyte batteries, super capacitors, electrochemical sensors and electro-chromic windows [1, 2]. Wright et al [3] and Armand [4] have reported that alkali metal salt association complexes with polyethylene oxide

have significant ionic conductivities. Apart from alkali metal salt-based polymer electrolytes, silver ion conducting polymer electrolytes based on host polymers such as polyethylene oxide [5–8], polyacrylamide [9] and polyvinylpyrrolidone [10] have also been reported. These silver ion conducting polymers have high ionic conductivities, of the order of  $10^{-5} \text{ S cm}^{-1}$  at ambient temperature, which may lead to new advances in rechargeable batteries. However, a literature survey reveals that there are only a few reports on polyvinyl alcohol complexed with silver ion, and investigations into the detailed mechanism of ion transport in these materials remain scarce. However, Armand has suggested that in crystalline polymer-salt complexes the cation migrates in a helical tunnel [11], and in the amorphous materials the cation moves from one site to the next by a free volume mechanism [4]. The AC impedance spectroscopic technique is an excellent tool for characterizing the electrical properties of the materials, and it may also be used to investigate the ion dynamics of bound or mobile charges of the materials [12, 13]. In the present work, a polymer electrolyte based on polyvinyl alcohol doped with silver nitrate is reported on, and ion dynamic studies have been carried out using AC impedance spectroscopic studies, and the results from these are presented in this paper.

### Experimental

Thick films of polymer electrolyte (400 μm) of pure polyvinyl alcohol (Merck,  $M_w = 1,25,000$ ) and polyvinyl alcohol doped with silver nitrate (Merck) with different compositions were prepared in the weight ratios (90:10), (80:20) and (70:30) by solution cast technique. Aqueous solutions of polyvinyl alcohol and AgNO<sub>3</sub> mixtures were thoroughly stirred for 10–12 h to obtain homogeneous mixtures. The mixtures were then poured on to a glass plate and evaporated slowly at room temperature. The final product was then vacuum dried. The IR spectrum was recorded for a polymer film in the range

G. Hirankumar · S. Selvasekarapandian (✉)  
M. S. Bhuvanewari · R. Baskaran · M. Vijayakumar  
Solid State and Radiation Physics Laboratory,  
Department of Physics, Bharathiar University, Coimbatore,  
641046, India  
E-mail: sekarapandian@yahoo.com  
Tel.: +91-422-2422222  
Fax: +91-422-2422387

of 400–4000  $\text{cm}^{-1}$  at room temperature using a SHIMADZU-8000 FT-IR Spectrophotometer. The electrical conductivity study of the polymer electrolyte was carried out in the temperature range of 303–373 K over a frequency range of 42 Hz–5 MHz using a computer-controlled HIOKI 3532 LCR meter with a cell with aluminum electrodes.

## Results and discussion

### FT-IR spectroscopy analysis

FT-IR spectroscopy is important to the investigation of polymer structure, since it provides information about the complexation and interactions between the various constituents in the polymer electrolyte. FT-IR spectra of the starting materials PVA,  $\text{AgNO}_3$  and of the polymer complex are shown in Fig. 1. The absorption peaks of PVA at 3372, 2925, 1430 and 1326  $\text{cm}^{-1}$  are assigned to O–H stretching, C–H stretching,  $\text{CH}_2$  wagging, and C–OH plane bending, respectively. The absorption peaks of PVA at 3372, 2925, and 1430  $\text{cm}^{-1}$  get shifted to 3415, 2949, and 1454  $\text{cm}^{-1}$  in the polymer complex, respectively. This implies a specific interaction of the salt in the polymer matrix. The characteristic band appearing at 1080  $\text{cm}^{-1}$  is assigned to the C–OH stretching of PVA, which is shifted to a lower wavenumber (1051  $\text{cm}^{-1}$ ) in the polymer complex system. The absorption peak of  $\text{AgNO}_3$  at 800  $\text{cm}^{-1}$  gets shifted to 775  $\text{cm}^{-1}$  in the polymer complex. The vibrational bands pertaining to PVA at 835, and 917  $\text{cm}^{-1}$  are assigned to C–OH wagging and  $\text{CH}_2$  rocking, respectively. They are shifted to 882, and 1018  $\text{cm}^{-1}$  in the polymer complex. The characteristic peaks of  $\text{AgNO}_3$  at 1800, and 1430  $\text{cm}^{-1}$  are absent in the polymer complex system. The vibrational frequencies at 1153 and 414  $\text{cm}^{-1}$

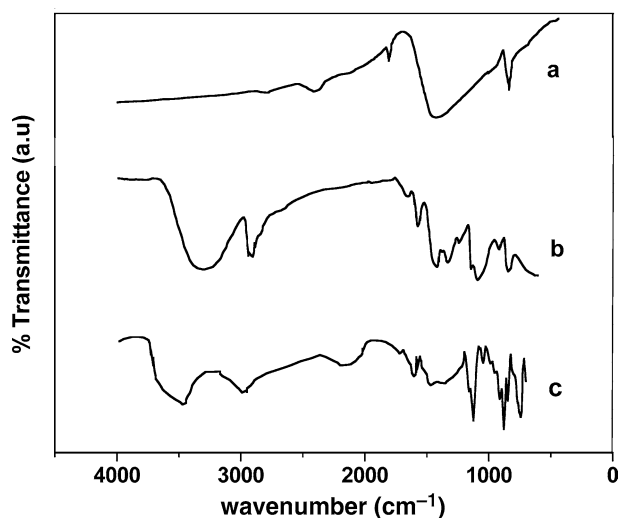


Fig. 1 FT-IR spectrum of (a)  $\text{AgNO}_3$ , (b) pure PVA and (c) 80% PVA + 20%  $\text{AgNO}_3$

in the polymer complex have been assigned to C–C stretching and  $-\text{CH}_2$ -stretching (chain expansion) vibrations, respectively [14]. The above analysis confirms the complexation of  $\text{Ag}^+$  ions in the host polymer.

### Conductivity analysis

The ionic conductivity of the polymer electrolyte as a function of salt concentration at room temperature is presented in Fig. 2. The ionic conductivity increases with increasing silver nitrate concentration, up to 20 wt%. The conductivity obtained at a salt concentration of 30 wt% indicates that the ionic conductivity decreases at higher salt contents. The increase in the ionic conductivity with increasing salt concentration can be related to an increase in the number of mobile charge carriers. The possible decrease in the ionic conductivity at salt concentrations greater than 20 wt% can be attributed to either incomplete dissociation of the salt or to the formation of ion multiples [15].

The conductivity as a function of temperature for pure polyvinyl alcohol and for different compositions of polyvinyl alcohol doped with silver nitrate with weight ratios 90:10, 80:20, 70:30 over the temperature range 303–373 K is shown in Fig. 3. The sample polyvinyl alcohol doped with 20 wt% silver nitrate exhibits the highest conductivity, as shown in Fig. 3. This can be attributed to the mobility of the  $\text{Ag}^+$  ion in the electrolyte. The activation energy for this system is found to be 0.35 eV. The variation of conductivity with temperature can be elucidated with the help of the Arrhenius equation, given below.

$$\sigma = (\sigma_0/T) \exp(-E_a/KT). \quad (1)$$

The experimental data indicate that the ionic conductivity is enhanced with increasing temperature. This

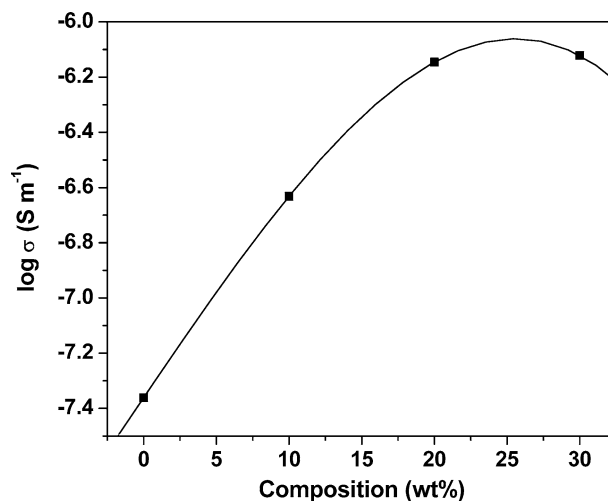
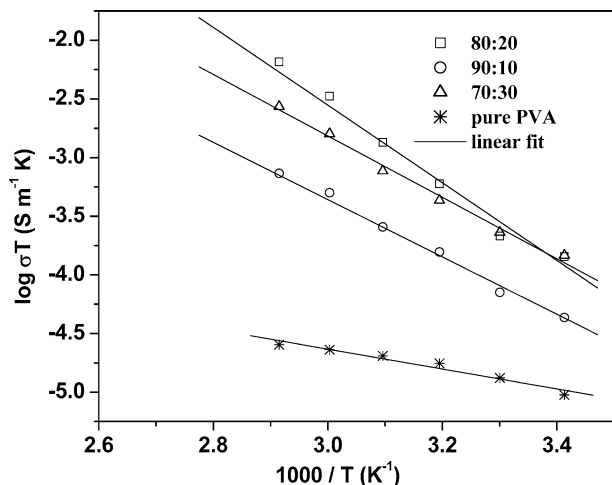


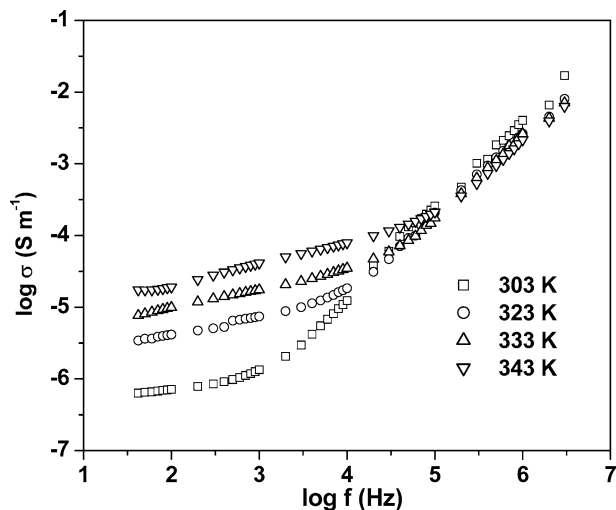
Fig. 2 Effect of the concentration of silver nitrate on the conductivity of polyvinyl alcohol at room temperature (303 K)



**Fig. 3** Conductivity as a function of temperature for polyvinyl alcohol +  $\text{AgNO}_3$  complexes

increase of conductivity with temperature can be explained on the basis of the ionic transport mechanism between coordinating sites, local structural relaxation and segmental motion of the polymer chain [16, 17]. When the temperature is increased, the mobility of the polymer chain is enhanced, and the fraction of free volume in the polymer electrolyte system increases accordingly, which facilitates the transitional motion of ions [18]. Thus the segmental motion either allows the ions to hop from one site to another site, or it provides a pathway for ions to move. Hence, the ionic motion in the polymer electrolyte is due to the hopping of ions from one site to another and the dynamic segmental motion of the polymer, which leads to an increase in the ionic conductivity of the polymer electrolyte. The transport parameters for the polymer electrolyte systems are summarized in Table 1.

The frequency dependence of the ac conductivity of the 20 wt% silver nitrate doped with PVA at different temperatures is shown in Fig. 4. The ac conductivity spectrum in Fig. 4 reveals that the conductivity is frequency-independent in the low frequency region, and is equal to the dc conductivity [19]. In the higher frequency domain, the conductivity increases as the frequency increases. However, at high frequencies, the conductivity is observed to be much less temperature-dependent than the dc conductivity. It is clear from Fig. 4 that the conductivity spectra obey Joncher's power law [20]:



**Fig. 4** Conductance spectra for the PVA +  $\text{AgNO}_3$  (80:20) system at different temperatures

$$\sigma_{ac}(\omega) = (\sigma_{dc}) + A\omega^\alpha, \quad (2)$$

where  $\alpha$  is the power law exponent. Both  $\sigma_{dc}$  and  $A$  are thermally-activated quantities.

According to the jump relaxation model reported by Funke [21], the power law exponent  $\alpha$  relates the backhop rate to the site relaxation time:

$$\alpha = \frac{(\text{backhop rate})}{(\text{site relaxation time})}. \quad (3)$$

If the ratio  $\alpha$  is less than one (so the backward hopping is slower than the site relaxation time), it results in translational motion of the  $\text{Ag}^+$  ion. However, if the ratio exceeds one, the backward hopping is faster than the site relaxation time. The conductivity spectra of the polymer electrolyte were fitted with Eq. 2 using a non-linear least-squares fitting procedure and the parameter  $\alpha$  was extracted and tabulated in Table 1. The  $\alpha$  value was found to be greater than one (1.24 and 1.06) for 10 and 30 wt% silver nitrate-added samples. This may be due to either the presence of a bad site for the next hop or to the coulombic repulsion between the mobile ions. The decrease in  $\alpha$  ( $=0.93$ ) for the 20 wt% silver nitrate-doped sample may be due to the formation of free sites for  $\text{Ag}^+$  ion transport, which indicates that the ions have a good site for their next hop and backward motion is slower due to less coulombic interaction between the ions [22].

**Table 1** Transport parameters for the polymer electrolyte

Sample	Conductivity ( $\sigma$ ) ( $\text{S m}^{-1}$ )		Activation energy (eV)		$\beta$	$\alpha$	Relaxation time $\tau$ (s)
	303 K	363 K	$E_m$	$E_a$			
PVA	$4.35 \times 10^{-8}$	$4.17 \times 10^{-7}$	—	—			
90%PVA + 10% $\text{AgNO}_3$	$2.34 \times 10^{-7}$	$3.20 \times 10^{-6}$	0.29	0.27	0.75	1.24	$4.8 \times 10^{-5}$
80%PVA + 20% $\text{AgNO}_3$	$7.56 \times 10^{-7}$	$3.00 \times 10^{-5}$	0.37	0.35	0.70	0.93	$4.1 \times 10^{-5}$
70%PVA + 30% $\text{AgNO}_3$	$7.15 \times 10^{-7}$	$1.48 \times 10^{-5}$	0.30	0.24	0.72	1.06	$1.0 \times 10^{-5}$

## Modulus analysis

Conductivity relaxation parameters have been calculated from the complex modulus formalism  $M^* = 1/j(\omega C_0) Z^*$ , where  $C_0$  is the capacitance of the cell in vacuum. Plots of normalized modulus ( $M''/M''_{\max}$ ) versus  $\log f$  at different temperatures for the composition corresponding to the 80:20 system are given in Fig. 5. The imaginary part of the electric modulus ( $M''$ ) as a function of frequency shows an asymmetric peak whose position is shifted towards higher frequencies with rising temperature. This behavior suggests that the relaxation is activated thermally, and charge carrier hopping is taking place. The angular frequency  $\omega_{\max}$  which corresponds to  $M''_{\max}$  gives the relaxation time,  $\tau_c$ , from the condition  $\omega_{\max} \tau_c = 1$  [23]. The migration energy  $E_m$  is estimated [24, 25] using the following equation:

$$\omega_m = \omega_0 \exp(-E_m/kT), \quad (4)$$

where  $E_m$  is the ionic migration energy.

The temperature dependence of the peak frequency  $\omega_{\max}$  is shown in Fig. 6. The migration energy for the ion in polymer electrolyte was calculated using the least-squares method and found to be 0.37 eV, which is in good agreement with the dc conductivity activation energy  $E_a$ . This result suggests that the charge carriers responsible for both conductivity and relaxation are the same, and that the enthalpy of carrier formation is negligible in this system. The non-symmetric curve is in agreement with the non-exponential behavior of the conductivity relaxation, which is described by the Kohlrausch function [26]  $\phi(t) = \phi_0 \exp(-t/\tau)^\beta$ . ( $0 < \beta < 1$ ), where  $\tau$  and  $\beta$  are the conductivity relaxation time and the Kohlrausch exponent, respectively. The  $\beta$  parameter corresponding to all of the composition was calculated using the formula  $\beta = 1.14/\text{FWHM}$ . The  $\beta$  values indicate the non-Debye nature

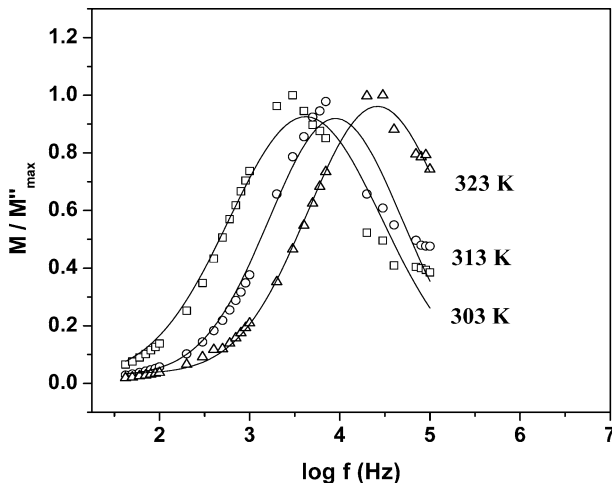


Fig. 5 Normalized modulus spectra of the electrolyte at various temperatures

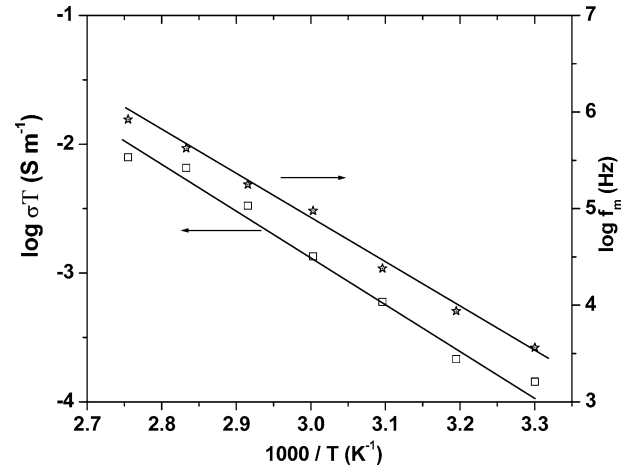


Fig. 6 Temperature dependence of  $\log \sigma T$  and  $\log f_m$

of the materials. The low value of  $\beta$  for the 80:20 system indicates lower coulombic repulsion between the charge carriers than in the other systems, which gives the high conductivity of the sample. This is in good agreement with the results from the conductance spectra analysis of the sample.

## Dielectric analysis

The dielectric properties of any system may be characterized by frequency-dependent parameters that can be defined by the complex permittivity  $\epsilon$ . The complex permittivity or dielectric constant of a system is defined by

$$\epsilon = \epsilon' - j\epsilon'' \quad (5)$$

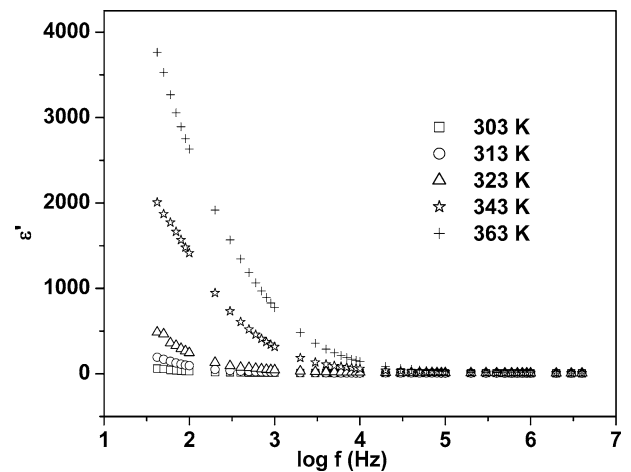


Fig. 7 Dielectric spectra for the polymer electrolyte (80:20) at various temperatures

The real and imaginary part of complex permittivity are of particular significance for an ion conducting polymer. Figure 7 shows the frequency dependence of the real part of the complex permittivity at different temperatures of the polymer electrolyte system (80:20). This shows that the low frequency dispersions are very strong and can be associated with space charge polarization effects arising from the electrodes. In the high frequency region, due to high periodic reversal of the field at the interface, the contribution of charge carriers towards the dielectric constant decreases with increasing frequency. Hence,  $\epsilon'$  decreases with increasing frequency.

---

## Conclusion

Thick polymer electrolyte films of pure polyvinyl alcohol and PVA doped with silver nitrate with different compositions were prepared by a solution cast technique. The FT-IR spectrum confirms the complexation of the polymer electrolyte. It has been observed that the system comprising polyvinyl alcohol doped with 20 wt% silver nitrate has the highest conductivity. The activation energy of the dc conductivity is very close to that of the migration energy, suggesting that the enthalpy of carrier formation is negligible in the present system. From the modulus and conductance spectra it may be concluded that the charge carrier responsible for both conductivity and relaxation are the same. Modulus analysis shows the non-Debye nature and distribution of relaxation times.

---

## References

1. Pantaloni S, Passerini S, Scrosati B (1987) *J Electrochem Soc* 134:753

2. Armand MB (1986) *Annu Rev Mater Sci* 16:245
3. Fenton BE, Parker JM, Wright PV (1973) *Polymer* 14:589
4. Armand M, Chabagno JM, Duclot MJ (1979) In: Vashishta P, Mundy JN, Shenoy GK (eds) *Fast ion transport in solids*. North-Holland, New York, p 131
5. Rao SS, Rao KVS, Sharefuddin M, Rao UVS (1994) *Solid State Ionics* 67:331
6. Abrantes TM, Alcacer LJ, Sequeira CAC (1986) *Solid State Ionics* 18(19):315
7. Chandra S, Hashmi SA, Saleem M, Agarwal RC (1993) *Solid State Ionics* 67:1
8. Rao SS, Rao KVS, Sharefuddin Md, Rao UVS, Chandra S (1994) *Solid State Ionics* 67:331
9. Rao SS, Rao UVS (1994) *Mater Sci Lett* 13:1771
10. Jaipal Reddy M, Rao SS, Laxminarsiah E, Rao UVS (1995) *Solid State Ionics* 80:93
11. Armand M, Chabagno JM, Duclot MJ (1978) Extended abstracts. In: *Second Int Conf on Solid Electrolytes*, 20–22 Sept 1978, St Andrews, Scotland
12. Macdonald JR, Kenan WR (eds)(1978) *Impedance spectroscopy: emphasizing solid materials and systems*. Wiley, New York
13. Vijaykumar M, Selvasekarapandian S, Bhuvanewari MS, Hirankumar G, Ramprasad G, Subramanian R, Angelo PC (2003) *Physica B* 334:390–397
14. Vien DL, Colthup NB, Fately WG, Grasselli JG (1991) *Infrared and Raman characteristic frequencies of organic molecules*, Academic, New York, p 85
15. Takahashi Y (1973) *J Polym Sci* 11:213
16. Vincent CA (1987) *Prog Solid State Chem* 17:347
17. Steele BCH, Weston SE (1981) *Solid State Ionics* 2:347
18. Miyamoto T, Shibayama K (1973) *J Appl Phys* 44:5372
19. Siekierski M, Wieczorek W, Przulski J (1998) *Electrochim Acta* 43:1339
20. Joncher AK (1977) *Nature* 267:673
21. Funke K, Roling B, Lange M (1998) *Solid State Ionics* 105:195
22. Vijaykumar M, Hirankumar G, Bhuvanewari MS, Selvasekarapandian S (2003) *J Power Sources* 117:143
23. Macedo PB, Moynihan CT, Bose R (1972) *Phys Chem Glasses* 13:171
24. Sayed MB (1992) *J Phys Chem Solids* 53:1041
25. Sayed MB (1996) *Zeolites* 16:157
26. Williams G, Watts DC (1970) *T Farad Soc* 66:80