Compensation Effect in the Electrical Conduction Process in Polyene Incorporated Lipid Films

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Phosphatidylcholine films doped with polyenes show compensation behavior at low polyene concentration and follow a three constant semiconduction equation $\sigma_T=\sigma_0' \exp(E/kT_0) \exp(-E/kT)$, σ_0' and T_0 being constants for the lipid and the other parameters having their usual meanings. Consistent values of the constants σ_0' and T_0 obtained from various methods of evaluation suggest that the compensation effect has a physical origin. Significant change in the semiconduction activation energy of lipid film on various polyene doping suggests strong lipid-polyene interaction in the doped films.

In our earlier communications we have demonstrated the validity of the compensation rule in the electrical conduction process in some polyenes[1,2] and nucleic acid bases.[3,4] In polyenes, the semiconduction activation energy was varied by chemical vapour adsorption whereas in nucleic acid bases such variation was attained by doping with acridine dyes at low concentrations.

It has been shown that these organic semiconductors satisfy the three constant equation

$$\sigma_T = \sigma_0' \exp(E/kT_0) \exp(-E/kT) \qquad (1)$$

where the preexponential factor σ_0 in the conventional expression has been replaced by $\sigma_0' \exp(E/kT_0)$. Here T_0 and σ_0' are constants for a specific material. The dependence of T_0 and σ_0' on the number of chemical double bonds,[5,6] donor and/or acceptor concentration in complexes,[3,4] molecular substituent groups[2] and molecular geometry[7] has been demonstrated. In Eq. 1 we have not used a half energy as was originally done by Rosenberg as localized states generally dominate in wide band gap materials like organic semiconductors and consequently it is more realistic to write down the activation energy according to the convention of extrinsic semiconduction.

However, some reported experimental results on compensation effect have often been criticized as these cover a narrow temperature range. Also the demonstrated compensation effect cover the Ohmic conduction region only. In pure and polyene doped phosphatidylcholine films sandwiched between a conducting SnO_2-coated glass and a stainless steel electrode, the conduction is known to be due to Schottky mechanism.[8] Also, this being a stable system, we have been able to cover a wider temperature range making the $\log \sigma_T$ vs. $1/T$ plots more meaningful in the context of compensation behavior. The result presented in this paper is therefore thought to add further credence to the physical origin of compensation effect.

Electrical conduction of model lipid membrane has been studied extensively in bilayers[9,10] and in thin films.[11,12] Light mediated electrical properties of some polyene incorporated bilayer lipid membranes have been studied extensively by Tien and his coworkers.[13-16] Dark conductive properties of the films was, however, neglected by them. This study is thought worthwhile also because the semiconductive properties of pure and polyene doped phosphatidylcholine, which is a major constituent of many cell membranes, is of significant relevance to olfactory transduction mechanism[17] where carotenoids incorporated in the olfactory cell membranes are thought to be the receptors of olfactory signals.

Experimental

Highly purified (99%) hydrogenated L-α-phosphatidylcholine (Egg lecithin) in powder form was obtained from Sigma Chemicals Co. U. K. High quality β-carotene, astacin, and vitamin A alcohol were obtained as gift from Hoffman La Roche Co. Switzerland. These materials, after checking purity by absorption spectroscopy, were used without any further purification. Each polyene was mixed with phosphatidylcholine in ca. 10^{-2} wt/wt concentration and ground repeatedly in a mortar till a uniform mixture was obtained. This mixed sample in powder form was taken in a sandwich cell configuration between a stainless steel and a SnO_2-coated glass electrode separated by a 2 mil (1 mil=0.0254 mm) thick Teflon spacer and pressed moderately to get a uniform thin film. The cell was then placed in a suitably designed conductivity chamber.[1] A dc voltage of 25 V across the electrodes was supplied from a dry battery pack. Currents were measured by an electrometer amplifier (model EA 815) of ECIL, India. Temperature measurements were made by a copper-constantan thermocouple and a panel meter (model 100) of HIL, India.

Results and Discussion

The semiconduction activation energies of all the samples were measured several times under vacuum (10^{-3} Torr; 1 Torr≈133.322 Pa) as well as in dry nitrogen atmosphere. All measurements gave consistent values. Almost the same values were obtained in vacuum and in dry nitrogen. The current-voltage characteristics of all the samples show Schottky behavior in the experimental voltage regime. The room temperature conductivity of the pure lipid

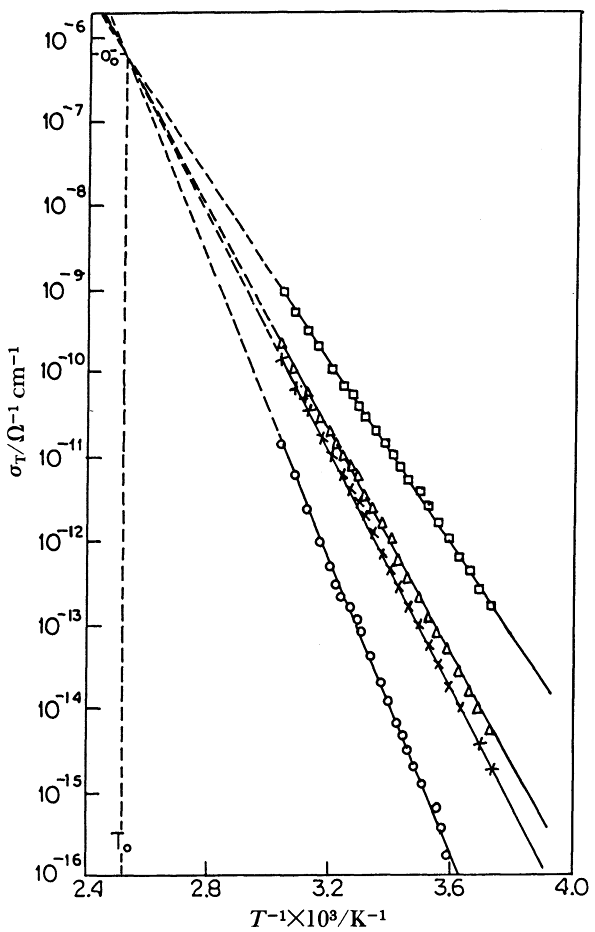

Fig. 1. The plot of $\log\sigma_T$ vs. $1/T$ for pure (—○—), β-carotene doped (—△—), vitamin A alcohol doped (—□—), and astacin doped (—×—) phosphatidylcholine films.

is ca. $10^{-13}\ \Omega^{-1}cm^{-1}$. With polyene incorporation this value increases and the activation energy (which is 1.74 eV for the pure lipid) decreases. Such increase in conductivity of lipid films after polyene incorporation may be attributed to strong lipid-polyene interactions which may be of dipole-dipole,[18] hydrophobic or donor-acceptor[19] type. Donor-acceptor interactions increase the conductivity of lipid membrane on I_2 or water adsorption.[20]

In Fig. 1 we show $\log\sigma_T$ vs. $1/T$ plots for pure and β-carotene, astacin, and vitamin A alcohol doped lipid films. It is seen that the extrapolated lines in these plots intersect the ordinate at a wide variety of positions but they all pass approximately through a single point at a temperature T_0. This result is in conformity with Eq. 1. At the characteristic temperature T_0, the value of σ gives σ_0' value. For phosphatidylcholine, value of T_0 is 396.8 K and $\sigma_0'=7.5\times10^{-7}\ \Omega^{-1}$ cm^{-1}. From Eq. 1 at any specific experimental temperature T_1, we get

$$\sigma(T_1)=\sigma_0'\exp(1/T_0-1/T_1)\,E/k \qquad (2)$$

$\sigma(T_1)$ will show different behavior with variation of E depending on whether $T_1>T_0$ or $T_1<T_0$. In our case $\sigma(T_1)$ increases with decreasing E as $T_1<T_0$.

Phosphatidycholine mixed with three different polyenes, β-carotene, astacin, and vitamin A alcohol has a distinct T_0 value. This result confirms our earlier observation[1,3] that T_0 is a molecular property of the semiconducting material.

Conpensation effect in the electrode limited conduction process has been discussed by Green.[21] He considered charge carrier injection at the semiconductor surface and showed that the preexponential factor in the standard semiconduction equation

$\sigma_T=\sigma_0\exp(-E/kT)$ is given by

$$\sigma_0\approx n_0\left(\frac{kT}{h}\right)K \qquad (3)$$

where n_0 is the number of carriers available at the electrode and K is the transmission coefficient. If E is the energy obtained from the $\ln\sigma$ vs. $1/T$ plots and is small compared to the work-functions of the electrode and the semiconductor, then one gets

$$\ln K=A+BE+CE^2 \qquad (4)$$

where A; B, and C are some parameters. Neglecting the quadratic term

$$\log\sigma_0\approx C+C'E \qquad (5)$$

where C and C' are related to the parameters A and B. σ_0 represents the first two terms of Eq. 4. The compensation temperature T_0 of Eq. 4 is related to C' which in turn is related to the difference of the work functions of the electrode and the semiconductor and potential barrier width.

Roberts and Polanco[22] showed that for appropriate parameters, thermally assisted tunneling (TAT) yields the same shape of current voltage characteristics as in Schottky effect. It has been shown by Roberts[23] that for TAT, $\ln\sigma_{TAT}$(max) vs. $1/T$ yields activation energy $E_{max}=\Phi-F_x$ where Φ is the potential barrier at the electrode-semiconductor interface and $F_x=(F/kT_x)^2$ $h^2/8m$ where F is the applied field and T_x is an arbitrary temperature. The curves at different F values pass through a focal point $T_0=(3/2)T_x$, where T_x is temperature corresponding to the average of the reciprocal temperatures through which experimental data points are collected. From Fig. 1, T_x=294 K and so the estimated T_0 value is 441 K. This is a value far beyond our experimental value which is ca. 400 K and is not within possible experimental error. Also for the TAT model proposed by Roberts,[23] the activation energy value should be temperature dependent and over an extended temperature range, the curves should deviate from the straight line. Our experimental results are at variance with this hypothesis. We therefore conclude that the thermally assisted tunneling model of Roberts cannot account for the obtained compensation effect in polyene doped lipid films.

True compensation effect is thought to arise from the existence of a linear relationship between the

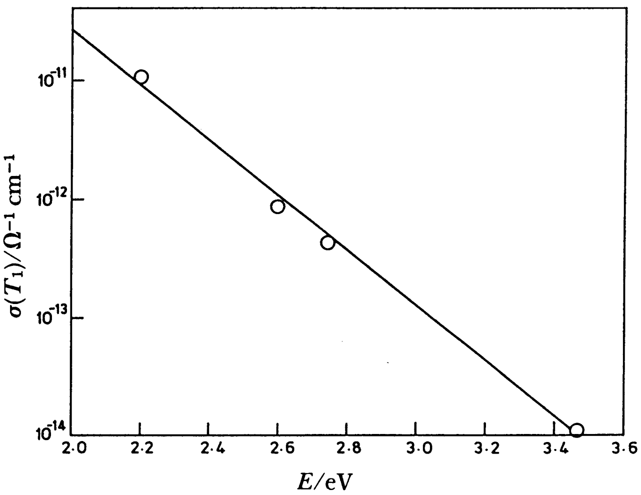

Fig. 2. The plot of $\log \sigma(T_1)$ vs. E at T_1=333.3 K for different polyene doped phosphatidylcholine films.

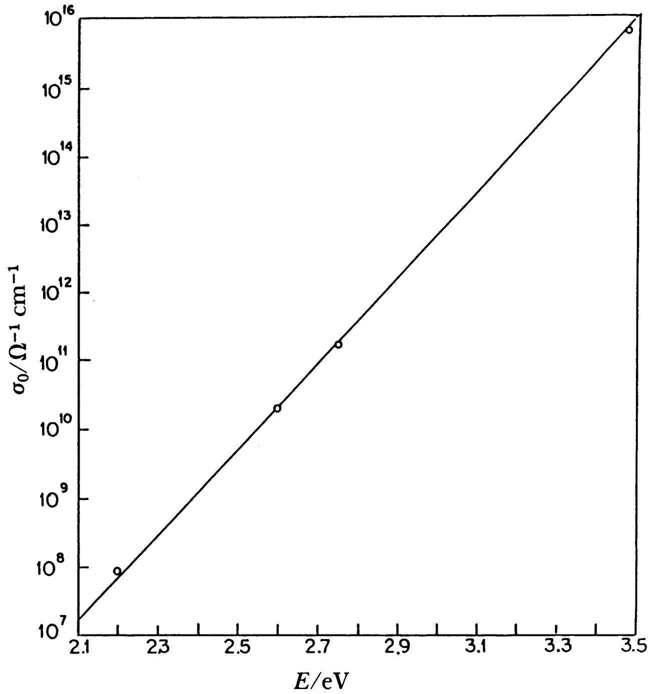

Fig. 3. The plot of $\log \sigma_0$ vs. E for different polyene doped phosphatidylcholine films.

activation energy and the activation entropy of the system. It has been pointed out by Johnston and Lyons[24] that if a true linear free energy relation (LFER) does hold for dark conduction. a physical relationship between σ_0 and E, $\log \sigma(T_1)$ vs. E must also be linear. In Fig. 2 we show such plot. T_0 and σ_0' are obtainable from the slopes and intercepts of these plots. These parameters can also be obtained from the plot of $\log \sigma_0$ vs. E as $\log \sigma_0 = \log \sigma_0' + E/kT_0$, σ_0 and E being experimentally measured. In Fig. 3 we show such plot. T_0 and σ_0' can be evaluated respectively from the slope and the intercept of this plot. In Table 1 we compare the values of T_0 and σ_0' obtained by various methods. The agreement is quite satisfactory. These results confirm that σ_0 and E are physically related and that T_0 has a physical origin. The meaning of T_0, however, remains unsettled. It has been established that T_0 is a molecular property of the semiconducting material.[25] In the theory based on rate process[26] T_0 has been attributed to the temperature at which the competing effects of energy and entropy balance each other.

Conclusion

The experimental results indicate that the compensation law is valid for electrical conduction process in various polyene doped phosphatidylcholine films where the conduction mechanism is electrode limited. Significant change in semiconduction activation energy of p lipid films on various polyene doping

Table 1. Comparison of T_0 and σ_0' Values of Pure and Various Polyene Doped Phosphatidylcholine Films

Different parameter	Phosphati dylcholine	Phosphatidyl choline+ β-carotene	Phosphatidyl choline+ astacin	Phosphatidyl choline+vitamin A alcohol
E/eV	1.74	1.30	1.38	1.10
σ_T/Ω^{-1} cm^{-1}	1.20×10^{-13}	5.60×10^{-12}	3.00×10^{-12}	4.50×10^{-11}
σ_0/Ω^{-1} cm^{-1}	6.46×10^{15}	1.88×10^{10}	1.70×10^{11}	8.50×10^{7}
σ_0'/Ω^{-1} cm^{-1} from Fig. 1.	←	7.50×10^{-7}		→
σ_0'/Ω^{-1} cm^{-1} from Fig. 2.	←	1.20×10^{-6}		→
σ_0'/Ω^{-1} cm^{-1} from Fig. 3.	←	8.90×10^{-7}		→
T_0/K from Fig.1	←	396.8		→
T_0/K from Fig.2	←	402.5		→
T_0/K from Fig.3	←	399.8		→

suggests strong lipid-polyene interaction as has been evidenced[13,14,27] from spectroscopic and other studies.

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