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ACTIVATION ENERGY: PLAYS AN IMPORTANT ROLE IN A CHEMICAL REACTION

Ashoke Hazra*

A.K.P.C. Mahavidyalaya, Subhasnagar, Bengai, Hooghly, West Bengal, India.

ABSTRACT

The present work describes how activation energy changes in Poly-Ethylene Oxide- based mixed solid polymer electrolyte(SPE) which are broadly applied in Lithium or Li-ion battery. Here we take three different temperatures such as 15^0C, 28^0C and 40^0C and five different single or mixed electrolytes. Ionic conductivities of the mixed SPE's are found to be slightly greater than those of single SPE's. log sigma Vs. 1/T plots indicate Arrhenius type behavior with activation of transport around 17 Cal. This plot (Arrhenius type behavior) shows that in case of mixed electrolyte, activation energy decreases and as well as ion conductivity increases than that of single electrolyte.

Key words: Activation energy, Lithium battery, Li-ion battery, Solid polymer electrolyte, conductivity, Arrhenius plot.

INTRODUCTION

The **Arrhenius equation** is a simple but remarkably accurate formula for the temperature dependence of reaction rates. The equation was proposed by Arrhenius, based on the work of Dutch chemist Van,t Hoff who had noted that Van,t Hoff equation for the temperature dependence of equilibrium constants suggests such a formula for the rates of both forward and reverse reactions. Arrhenius provided a physical justification and interpretation for the formula [1-3]. Currently, it is best seen as an empirical relationship [4]. It can be used to model the temperature variation of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions. The Erying equation, also expresses the relationship between rate and energy.A historically useful generalization supported by Arrhenius' equation is that, for many common chemical reactions at room temperature, the reaction rate doubles for every 10 degree Celsius increase in temperature.

Arrhenius' equation gives the dependence of the rate constant $k$of a chemical reaction on the absolutetemperature T(in Kelvin), where is the pre-exponentialfactor (or simply the *prefactor*), $E_a$is the activation energy, and $R$is the universal gas constant.

$$k = Ae^{-E_a/(RT)}$$

Alternatively, the equation may be expressed as

$$k = Ae^{-E_a/(k_BT)}$$

The only difference is the energy units of E_a: the former form uses energy per mole, which is common in chemistry, while the latter form uses energy per molecule directly, which is common in physics. The different units are accounted for in using either R= gas constant or the Boltzmann constant k_B as the multiplier of temperature T.

The units of the pre-exponential factor $A$are identical to those of the rate constant and will vary depending on the order of the reaction. If the reaction is first order it has the unit s^{-1}, and for that reason it is often called the frequency *factor* or *attempt frequency* of the reaction. Most simply, $k$is the number of collisions that result in a reaction per second, $A$is the total number ofcollisions (leading to a reaction or not) per second and $e^{-E_a/(RT)}$is the probability that any given collision will result in a reaction.

Corresponding Author:-**AshokeHazra** Email: hazra.ashoke@gmail.com

It can be seen that either increasing the temperature or decreasing the activation energy (for example through the use of catalyst) will result in an increase in rate of reaction.

Given the small temperature range kinetic studies occur in, it is reasonable to approximate the activation energy as being independent of the temperature. Similarly, under a wide range of practical conditions, the weak temperature dependence of the pre-exponential factor is negligible compared to the temperature dependence of the $\exp(-E_a/RT)$ factor; except in the case of "barrier less" diffusion-limited reactions, in which case the pre-exponential factor is dominant and is directly observable.

Arrhenius plot

Taking the natural logarithm of Arrhenius' equation yields:

$$\ln(k) = \frac{-E_a}{R}\frac{1}{T} + \ln(A)$$

This has the same form as an equation for a straight line:

$$y = mx + c$$

So, when a reaction has a rate constant that obeys Arrhenius' equation, a plot of ln(*k*) versus T^{-1} gives a straight line, whose gradient and intercept can be used to determine E_a and *A* . This procedure has become so common in experimental chemical kinetics that practitioners have taken to using it to *define* the activation energy for a reaction. That is the activation energy is defined to be (-*R*) times the slope of a plot of ln(*k*) vs. (1/*T*)

$$E_a \equiv -R\left[\frac{\partial \ln k}{\partial\,(1/T)}\right]_P$$

Arrhenius argued that for reactants to transform into products, they must first acquire a minimum amount of energy, called the activation energy E_a. At an absolute temperature *T*, the fraction of molecules that have a kinetic energy greater than E_a can be calculated from statistical mechanics. The concept of *activation energy* explains the exponential nature of the relationship, and in one way or another, it is present in all kinetic theories.

The calculations for reaction rate constants involve an energy averaging over a Maxwell Boltzmann Distribution with E_a as lower bound and so are often of the type of incomplete gamma functions, which turn out to be proportional to $e^{\frac{-E_a}{RT}}$.

Experimental

Materials

Poly(ethylene oxide) (BDH, USA) with an approximate molecular weight $6\text{x}10^5$, $LiNO_3$(E MERCK) and $LiClO_4$(Lancaster, England) were used as suchwithout any further purification. Li-Picrate was prepared by the procedure reported previously [5]. Acetonitrile (BDH) was purified by successive distillation from P_2O_5 and CaH_2 after initial drying with CaH_2 [6].

Electrolyte

Polymer complexes were prepared by dissolving PEO and lithium salt in acetonitrile at 8:1 mole ratio of EO:Li. Here $LiClO_4$, LiPic and $LiNO_3$ salts are used for the preparation of SPE. The composition of the SPE's i.e, PEO: Salt ratio has been kept same as our earlier studies [7-8] with SPE's are well justified. Then the solutions were properly mixed for 7 to 8 hours at 308 to 313 K in stoppered condition. The clear solution was then sprayed on a glass slide, the edge of which was covered by strip of PEO. The solvent was evaporated under reduced pressure at room temperature and the slides were kept in dessicator for several days.

PEO based mixed SPE's were prepared by the same procedure at same mole ratio of EO:Li.The film thickness of the SPE's were measured by using micrometer (Mitutiyo, Japan) and the ionic conductivities by four probe technique [9].The average film thickness of these SPE's are 190-200 µm.

RESULT AND DISCUSSIONS

Ionic conductivity of PEO based mixed polymer electrolytes at 8:1 mole ratio at different temperatures (288K to 313K) are shown in Table 1. It may be noted that ionic conductivities of mixed electrolytes are significantly increased compared to the single electrolyte SPE. The ionic conductivities of these SPE's follow the sequence PEO-($LiClO_4$+LiPic)> PEO-($LiClO_4$+$LiNO_3$)> PEO-$LiClO_4$ > PEO-LiPic> PEO-$LiNO_3$.

Plot of log(Conductance) vs. 1/T (Fig 1) these electrolyte show Arrhenius type behavior with activation energy ranging from 11.62 Cal to 16.61 Cal. The relative orders of activation energy of ionic transport follow the reverse sequence of ionic conductivity. In the presence of mixed ions of different size, the polymer matrices become significantly loosening their structure. So, charge transfer or ion diffusion becomes easier. SEM study supports the loosening of mixed SPE's than the single SPE [10].

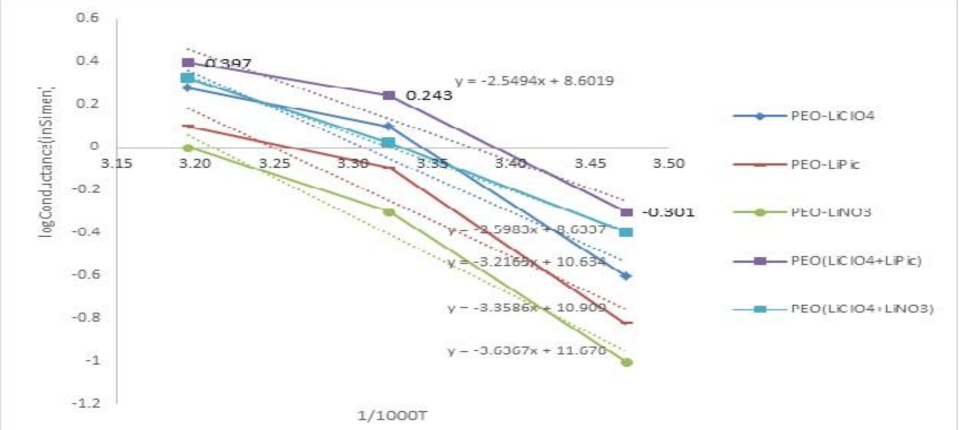
From Table 1 it has been found that different electrolyte show different conductivity as well as activation energy. If we go from single electrolyte to mixed electrolyte we have seen that ion conductivity increases from single electrolyte to mixed electrolyte. This is due to the fact that in the mixed electrolytes the salts appear to spread over the entire range of the polymer matrix almost uniformly. Thus crystallinity of single electrolyte loosen to some extent in case of the mixed electrolyte complex. Lower activation energy favours a chemical reaction with high ion conductance i.e, mobility of ions are increases as well as forward reaction increases.

This was observed in case of mixed SPE's. In case of single electrolyte activation energy is to some extent high which are not favour forward reaction. So, it can be concluded that activation energyplays an important role to conversion of reactant to product in a chemical reaction. Here we have observed this in case of solid polymer electrolyte (SPE) matrix's.

Table 1. Ionic conductivity and activation energy of PEO base single SPE and mixed SPE between 288-313K

Solid Polymer Electrolyte	Mole Ratio	Conductivity S ($cm^{-1}x10^5$) at			ΔE(Cal)
		288K	301K	313K	
PEO-$LiClO_4$	8:1	0.25	1.25	1.90	11.88
PEO-LiPic		0.15	0.80	1.25	15.36
PEO-$LiNO_3$		0.10	0.50	1.00	16.61
PEO-($LiClO_4$+LiPic)		0.50	1.75	2.50	11.62
PEO-($LiClO_4$+$LiNO_3$)		0.40	1.05	2.10	14.71

Figure 1. Plot of log Conductance Vs. 1/1000T (Arrhenius plot of PEO based SPE's between 288 to 313K)



CONCLUSION

Ionic conductivities of the mixed SPE's are found to be slightly greater than those of single SPE's. log sigma Vs. 1/T plots indicate Arrhenius type behavior with activation of transport around 17 Cal. This plot (Arrhenius type behavior) shows that in case of mixed electrolyte, activation energy decreases and as well as ion conductivity increases than that of single electrolyte. So, it may be concluded that activation energy of mixed SPE's are less than that of single SPE's which entirely controls the overall reaction. Thus, activation energy plays an important role to conversion of reactant to product in a chemical reaction. Here we have observed this in case of solid polymer electrolyte matrix's.

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