Studies of ion-pair to ionic dissociation of Li-Picrate salt in (PC+THF) at different mixtures with different temperatures

Abstract: Conductance of Li-Picrate was measured in different temperatures (250C, 350C, 450C). The limiting equivalent conductance (l0) and the ionassociation constant (KA) for Li-Picrate in (PC+THF) solvents at different percentage were evaluated using Debye-Huckel Onsager equation. It is observed that the limiting equivalent conductance increased linearly with the increase in temperature and the association constant values decreased with rise in temperature. Thermodynamic parameters (i.e, ıG0 , ıH0 , ıS0) are estimated from the temperature dependence of the ion-association constant . The positive values of ıS0 and positive values of ı H0 indicate the ion-association process occurred spontaneously as well as endothermic at all respective temperature. Supported by absorbance data from this primary study, it may be concluded that room temperature solubility of Li-Picrate in mixed (PC+THF) solvents at different percentage is higher than the higher temperatures. Conductivity data helps us to concluded that if we go from room temperature to higher temperature conductance increases for Li-Picrate in (PC+THF) solvents at different percentage. It is due to the switch over of ion-pair to ionic dissociation of Li-Picrate salt.

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1. Introduction

In continuation of our earlier study [1] on conductivity and solubility of Lipic in (PC+THF) mixture in different temperatures I report here to establish the earlier experiment with the help of thermodynamic parameters which will help us to application in Li-ion batteries. The measurement of electrical conductivities of the dilute solutions of salts or complexes are considered to be one of the important methods for studying the ion-pair or multiple–ion association not only in aqueous solutions but also in non-aqueous, or mixed ones [2-5]. The present work aims to determine the conductance values of Li-Picrate in different (PC+THF) non-aqueous mixtures have been measured at 25^0C, 35^0C and 45^0C to examine the validity of Debye-Huckel Onsager equation. The limiting equivalent conductance (λ0) and the ion-association constant (KA) have been evaluated.

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2. Experimental

2.1. Materials

PC (LOBA Chemicals), THF (PDFCL, Mumbai), Picric acid (LOBA Chemicals), Alcohol (Bengal Chemicals and Pharmaceuticals), Ether (LOBA Chemicals), Lithium Carbonate (LOBA Chemicals) were used as such without any further purification.

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2.2. Preparation of Li-Picrate (Li-Picrate) A small portion of Picric acid (LOBA Chemicals) was dissolved in minimum quantity of absolute alcohol (Bengal Chemicals and Pharmaceuticals). The solution was warmed at 40-50 degree Celsius. Lithium Carbonate (LOBA Chemicals) was added to the solution pinch by pinch (gradually decreasing amount) till the effervescence of carbon dioxide stops. Still it was kept at low

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2.3. Solutions Preparation

For the preparation of 20% (PC+THF) solution by v/v ratio, 2 c.c. PC and 8 c.c. THF have taken in a 50 c.c. stoppered bottle. Then a minimum amount of Li-Picrate has taken to it up to its saturation. Then it was sealed with wax. After waxing it was jerking for few minutes and then settled for 7 days. After 7 days, it was further jerked and settled. Then after 7 days the solution was filtered with whattmann-42 filter paper. At the same procedure 40% (PC+THF) solution with Li-Picrate have been prepared.

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2.4. Solubility Study

Solubility of the above solutions were measured with the help of Mini Spectrophotometer (SL-171, Elico) with spectral range 340-1000 nm and band width 5 nm. For this study, at first scanning was performed for Li-Picrate and after scanning the spectrum was fixed around 500 nm. Then the total observations were performed for Li-Picrate around 500 nm. Then the absorbance value was measured at 25 degree Celcius, 35 degree Celcius and 45 degree Celcius for different (PC + THF) solution with Li-Picrate (vide Table 2).

To get the unknown conc. of Li-Picrate , two known conc. of 0.1M and 0.05M were prepared. Knowing the absorbance value of 0.1M and 0.05M if we plot absorbance Vs. Conc., then we can get the unknown conc. of Li-Picrate solution with the help of calibration curve. Same calibration curves were used to get the unknown conc. of Li-Picrate from different percentage of (PC + THF) non-aqueous mixture at different temperatures (vide Table 3).

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2.5. Conductivity study

Conductivity of the above solutions were measured with a conductivity bridge (EC-TDS analyser, CM-183, Elico). Cell constants varied from 1.0+10% to 1.0-10% cm inverse. A temperature control bath (made by PDIC) was used to obtain the conductivities at the higher temperatures.

3.Result and discussions

The experimental data of conductance measurement of Li-Picrate in 20%, 40% (PC + THF) non-aqueous mixture at different temperatures were analysed using Debye-Huckel Onsager equation [10].

Since the conductance of an ion depends on its mobility, it is reasonable to treat the conductance data similar to the one that employs for rate processes taking place with temperature [6].

i.e, $\lambda 0 = A.\ e^{-\Delta Es/RT}$

or, $\ln \lambda 0 = \ln A - \Delta Es/RT$

Where 'A' is the frequency factor, R is the ideal gas constant and ΔEs is the Arrhenius activation energy of transport processes. From the plot of log λ0 vs. 1/T for this system in (PC + THF) non-aqueous mixture at different temperatures, the ΔEs value has been calculated from the slope [11] and tabulated in Table.1 and Fig. 1

Table 1 : Physical properties of Electrolyte solvents

Solvent	Structure	M.Wt.	Melting Temp.	Boiling Temp.	Viscisity at 25 ^{o} C	Dielectric constsnt at 25 ^{o} C	Dipole moment	Flash Temp.	Density(gm at 25 ^{o} C
PC		102	-48.8	242	2.53	64.92	4.81	132	1.200
THF		72	-109	66	0.46	7.4	1.7	-17	0.88

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Table 2: Absorbance of different(PC+THF) solution with Li-Picrate at different temperature

Temp	Percentage of solution	Absorbance of saturated solution	0.1M	0.05M
25 ^{o} C	20%	2.653	0.607	0.324
25 ^{o} C	40%	1.005	0.425	0.250
35 ^{o} C	20%	0.848	0.525	0.325
35 ^{o} C	40%	0.750	0.518	0.240
45 ^{o} C	20%	0.611	0.490	0.250
45 ^{o} C	40%	0.455	0.412	0.232

Table 3: Conc. of different % of solution at different temperature from calibration curve

Temp	Percentage of solution with saturated Lipic	Unknown Conc.(moles/litre)	0.1M	0.05M
25 ^{o} C	20%	0.4312	0.607	0.324
25 ^{o} C	40%	0.2284	0.425	0.250
35 ^{o} C	20%	0.1542	0.525	0.325
35 ^{o} C	40%	0.1469	0.518	0.240
45 ^{o} C	20%	0.1241	0.490	0.250
45 ^{o} C	40%	0.1077	0.412	0.232

Table 4. Thermodynamic parameters of Li-Picrate in (PC+THF) mixtures at different temperature for 20%

T(K)	$\lambda 0$ (µs)	KA	ΔH^0 (J/mole)	ΔG^0 (KJ/mole)	ΔS^0 (J/mole)	ΔEs (KJ/mole)
298		112.62	4651.7	-11.706	54.8925	
308	1063.1	16.89		-7.240	38.6106	23.124
318		11.93		-6.556	35.2450	

Table 5. Thermodynamic parameters of Li-Picrate in (PC+THF) mixtures at different temperature for 40%

T(K)	$\lambda 0$ (μs)	KA	ΔH^0 (J/mole)	ΔG^0 (KJ/mole)	ΔS^0 (J/mole)	ΔEs (KJ/mole)
298		49.22		-9.654	40.058	
308	1719.3	37.07	2282.4	-9.253	37.453	23.124
318		16.13		-7.353	23.194	

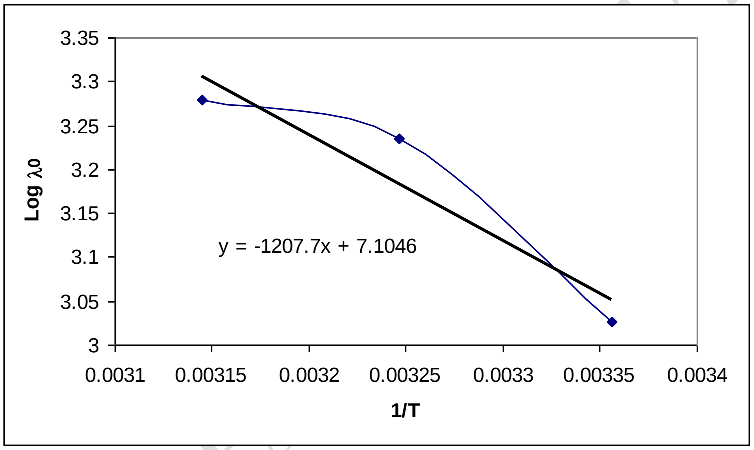

Fig.1. Plot of logλ0 vs. 1/T

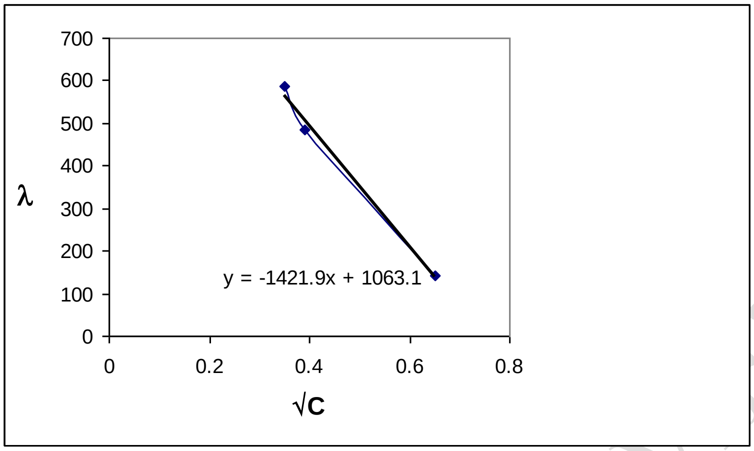

Fig.2. Plot of conductance(λ) Vs. √C of 20% (PC + THF).

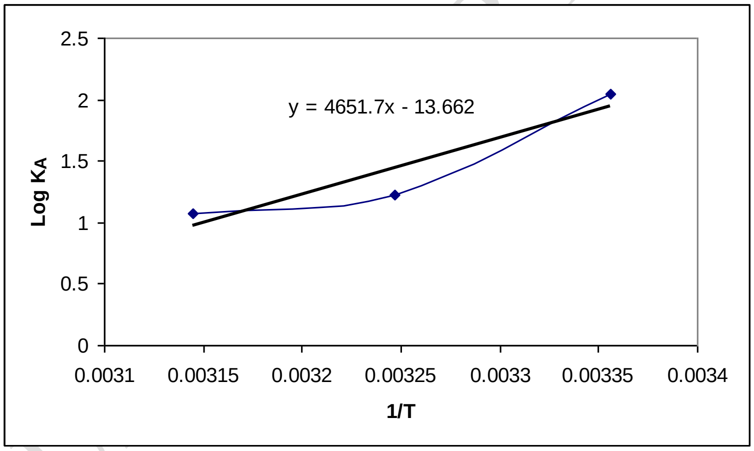

Fig.3. Plot of $\log K_A$ vs. 1/T of 20% (PC + THF).

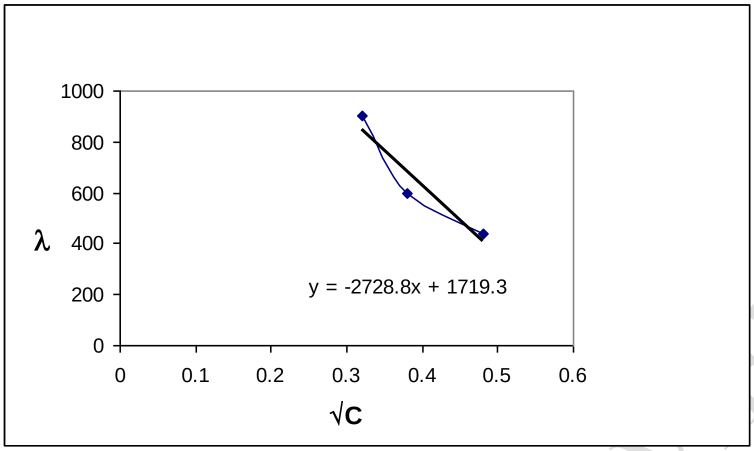

Fig.4. Plot of conductance (λ) Vs. √C of 40% (PC + THF).

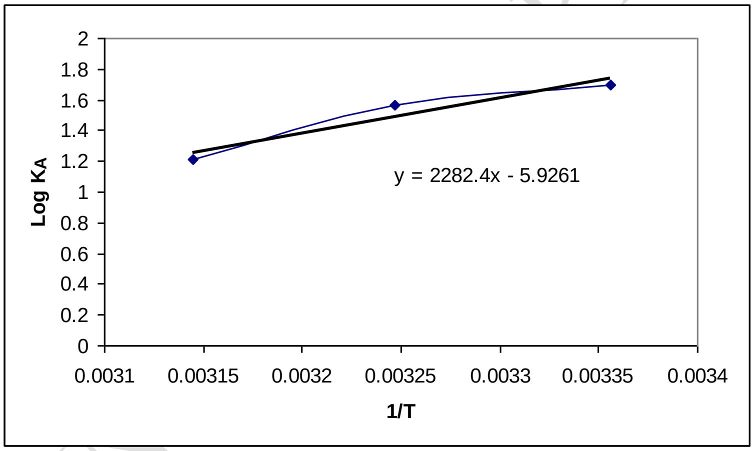

Fig.5. Plot of $\log K_A$ vs. 1/T of 40% (PC + THF).

From the Arrhenius equation it has been found that activation energy is positive. This indicates the higher mobilities of ions in solutions. It follows our basic concept that with increase in temperature mobilities of ions in solution increases. So, λ0 (limiting conductance) value increases with increase in temperature. But here we are studying at a particular temperature with different composition of Li-Picrate. So, from the temperature 25^0C to 35^0C , 45^0C value increases but at 45^0C, λ0 value decreases.

It was observed from our study for Li-Picrate with different (PC+THF) non-aqueous mixtures. The free energy change (ΔG^0) for association is calculated from the relation [12] ((ΔG^0 = -RT lnKA). The values of ΔG^0 at different temperatures are tabulated in Table 4, & 5 . (ΔG^0 values are obtained from the Fig. 2, 4 respectively. The heat of association (ΔH^0) is obtained from the slope of the plot of log KA vs. 1/T (Fig.3 & 5). The entropy change (ΔS^0) is calculated from Gibbs- Helmholtz equation (($\Delta G^0 = \Delta H^0 - T\Delta S^0$) from 2nd law of thermodynamics. The values of the thermodynamic parameters are shown in Table 4 & Table 5. At the three temperatures (25^0C , 35^0C & 45^0C) the positive value of ΔH^0 indicates that the ion association processes are endothermic in nature in the mix nonaqueous solvents with LiPic. At 25^0C, KA value decreases in (PC+THF) solution with LiPic and conductance value increases from lower to higher (PC+THF) solution with LiPic. At 35^0C, KA value also decreases from lower to higher but the value of KA too much increases from the 25^0C. This is due to the abrupt change of ion conductance of LiPic in (PC+THF) non-aqueous mixture. At 45^0C, KA value also decreases from lower to higher of LiPic in (PC+THF) non-aqueous mixture. ΔG^0 values are negative from 25^0C to 45^0C which indicates that the reactions are spontaneous. ΔS^0 values are also positive from 25^0C to 45^0C which indicates or supports that the reactions are also spontaneous. The effect of temperature (Table 4 to Table 5) can be noticed from decreasing the negative values of the associating free energies as the temperature is raised from 25^0C to 45^0C. From the above fact it can be told that the salvation increases as temperature increases as well as the association constant decreases. Limiting equivalent conductance (λ0) increases from 25^0C to 45^0C. But at 35^0C the value is too much high. At 20% solution from all the three temperatures KA increases i.e, salvation is less. Endothermic salvation needs energy to break the bonds around the free ion and ion-pairs i.e, ΔS^0 values are almost constant but ΔG^0 decreases the negativity with increasing the temperature. For mixed non-aqueous solve nts [1] this indicates that ion-pair association is favoured with lowering of dielectric constant (Table. 1) of the medium. A positive value of entropy change suggests that from lower to higher the disorderliness increases i.e, the spontaneity increases. KA value decreases with increase in temperature from lower to higher of LiPic in (PC+THF) non-aqueous mixture which is evident that the activation energy (Es) is positive and ΔG^0 negative value decreases as well as the ΔS^0 value decreases from lower to higher of LiPic in (PC+THF) nonaqueous mixture. The positive value of ΔS^0 indicates that the randomness increases from lower temperature to higher temperature. The main factors which govern the standard entropy of ion association of electrolytes are (i) the size and shape of the ions (ii) charge density of ions (iii) electrostriction of the solvent molecules around the ions and (iv) the penetration of the solvent molecules inside the space of the ions [13]. ΔS^0 value decreases from lower to higher and KA value decreases from lower to higher. This is also evident that association process is favoured rather than the dissociation process as well as randomness decreases from lower to higher solutions i.e, spontaneity decreases as the

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Commented [U25]: this statement is misleading dielectric constant of the mixture decreases. So, the salvation of ions weakens as well as the ion-pair formation occurs.

4.Conclusion

From the above study it may be concluded that $\lambda0$ increases with increase in temperature while KA value decreases with increase in temperature for the mixed nonaqueous solvents (PC+THF) with LiPic according to Debye Huckel Onsagar equation [10]. Thus from the plot of log $\lambda0$ vs. 1/T for this system in (PC + THF) non-aqueous mixture at different temperatures, the ΔEs value has been calculated from the slope. Thermodynamic parameters (i.e, ΔG^0 , ΔH^0 , ΔS^0) are estimated from the temperature dependence of the ion-association constant. It was found that ΔG^0 decreases the negativity with increasing the temperature which indicates the spontaneity of the nonaqueous reaction. The heat of association (ΔH^0) is obtained from the slope of the plot of log KA vs. 1/T. At all the three temperatures, the positive value of ΔH^0 indicates that the ion association processes are endothermic in nature in mixed non aqueous solvents (PC+THF) with LiPic. Ion association constant KA value decreases with increase in temperature for the mixed non-aqueous solvents (PC+THF) with LiPic from lower to higher conc of the solution. This is due to the switch over of ion-pair to ionic dissociation of LiPic from lower to higher. Some anomalous behaviour were observed in case of 35^0C. Here $\lambda0$ is too much high other than two different temperatures as well as the value of KA, ΔG^0 , ΔH^0 , ΔS^0. This is due to the very quick switch over from ion-pair to ionic dissociation of LiPic in (PC+THF) mixed non aqueous solvents. The ΔS^0 value decreases from lower to higher (PC+THF) mixed solvents with LiPic. The positive value of ΔS^0 indicates the randomness increases from lower temperature to higher temperature. The negative values of different thermodynamic parameters ΔG^0 , ΔH^0 , ΔS^0, for all salts under test in the used solvent, indicated exothermic association process was less energy consuming and more stabilized [14]. The entropy of ionization decreases slowly with increase in temperature. From this angle, the ionization should decrease with temperature. However, entropy alone is not the deciding factor. Also in the present case the entropy change is also low (only few Joules per mole). But the ultimate controlling factor is ΔG^0 which monotonically decreases for process of ionization which is –ve of the ΔG^0 value of the ionic association as shown in Table 4 and 5 with increasing temperature. So, the ionization increases with increasing temperature.

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Conductivity data helps us to concluded that if we go from room temperature to higher temperature conductance increases for Li-Picrate in (PC+THF) solvents at different percentage. It is due to the switch over of ion-pair to ionic dissociation of Li-Picrate salt.

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6. References

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