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Conductance, Dissociation Constant and Thermodynamic Parameters Studies of Succinic acid in Water + Pyruvate Carboxylase and Water + Tetrahydrofuran medium

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ABSTRACT

Present paper describes the conductivity studies of succinic acid with aqueous PC and THF medium. Limiting molar conductivities and dissociation constant (Kc) were calculated by Kraus-Bray conductivity equations from 288K to 318K. Thermodynamic parameters ΔH, ΔG, ΔS, ΔEs were calculated.

Keywords: Succinic acid, Conductivity, Pyruvate carboxylase, Tetrahydrofuran.

INTRODUCTION

In continuation our earlier studies¹⁻³ we focused in the present studies that how succinic acid solvated in water + PC and water + THF medium. Researchers interested in different weak acids in different solvent medium.

Study of conductance behaviour of aqueous and non-aqueous medium is much interest in recent past⁴⁻⁶.

As succinic acid is weak electrolyte, to determine limiting molar conductance was not measured by Onsagar equation. To determine limiting molar conductance we use Karus-Bray conductivity equation.

Many researchers studied the effect of

different salts and weak acids in different solvent systems⁷⁻¹⁵.

Our main objective to study to evaluate limiting molar conductance using Karus-Bray equation and also evaluate thermodynamic parameters for supporting the ion-solvation interaction system with this weak acid.

EXPERIMENTAL

Materials

Succinic acid (Merck), PC (LOBA Chemicals), THF(PDFCL, Mumbai) were used as such, without any further purification.

Solutions preparation

The solution of Succinic acid in water and different compositions (10%, 20%, 40%, 50%, 60%,

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80%) were prepared. Succinic acid solution (0.1M) was prepared in water, water + PC and water + THF in volume ratio(v/v).

Conductivity study

Conductivity of the above solutions were measured with a conductivity bridge (EC-TDS analyser, CM-183, Elico). Cell constant 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 temperature.

RESULT AND DISCUSSION

Molar conductance data was observed in different composition of succinic acid solution with (water + PC) and (water + THF). As succinic acid is weak electrolyte, to determine limiting molar conductance was not measured by Onsagar equation. To determine limiting molar conductance we use Karus-Bray conductivity equation.

The equation is $1/\lambda m = 1/\lambda m0 + \lambda mc/\lambda m02kc$ (i)

Where Kc = dissociation constant, C = conc. in mol/dm³, λm^0 = molar conductance at infinite dilution.

If we plot $1/\lambda m$ vs. λmC , we get λ_m^0 value from the intercept and from the slope, we can calculate Kc(dissociation constant).

Table 1 shows the the physical property data of the solvents PC and THF respectively.

Ka(association constant)'s were calculated from the limiting molar conductivities. Knowing the value of degree of association (a), Ka value can be easily calculated. With increase in Ka value, degree of dissociation decreases. With increase in % of succinic acid. Ka value decreases as well as dissociation increases.

Solvent	M. Wt	Melting Temp.	Boiling Temp.	Viscosity at 25ºC	Dielectric constant at 25ºC	Dipole moment	Flash Temp.	Density(gm/c.c.) at 25ºC
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

Table 1: Physical properties of Electrolyte solvents

		Та	able 4: Li	mitina m	olar conduct	ance of s	succinic	acid solv	vated in		
	-0.16	-0.28	-0.33	-0.28			-0.23	-0.21	-0.25	-0.23	
Slope	15ºC	25°C	35°C	45ºC	Water +PC	Slope	15ºC	25°C	35ºC	45°C	Water +THF

(Water +PC) and (Water + THF) medium from 288K to 318K

Serial no	Temp(in K)	1/T(K ⁻¹)	Water+ $PC(\lambda_m^{0})$	Water+ THF(λ_m^{0})
1	288K	0.0034	370.87	384.61
2	298K	0.0033	400.00	454.54
3	308K	0.0032	\1333.33	1666.66
4	318K	0.0031	1428.57	2000.00

Table 5: Dissociation constant, activation of solvation and different thermodynamic parameters of succinic acid solvated in (Water + PC) medium from 288K to 318K

Temp	Kc	$\Delta G(cal/mole)$	$\Delta S(cal/mole)$	$\Delta H(cal/mole)$	ΔEs(Kcal/mole)	$\lambda_m^{\ 0}$
288K	4.71	-892.75	-12.30	-2651.4	10.54	370.87
298K	3.96	-820.35	-11.64			400.00
308K	13.09	-1583.21	-13.74			1333.33
318K	15.28	-1734.21	-13.79			1428.57

ΔH, ΔG, ΔS, ΔEs

 Table 6: issociation constant, activation of solvation and different thermodynamic

 parameters of succinic acid solvated in Water + PC
 medium from 288K to 318K

Temp	Kc	$\Delta G(cal/mole)$	$\Delta S(cal/mole)$	ΔH(cal/mole)	ΔEs(Kcal/mole)	$\lambda_m^{\ 0}$
288K	4.53	-870.20	-6.45	-989.7	12.57	384.61
298K	3.83	-800.35	-6.00			454.54
308K	5.24	-1020.43	-6.52			1666.66
318K	8.72	-1377.55	-7.44			2000.00

Table 7: Ka(Association constant) values of succinic acid solvated in (Water + PC) medium from 288K to 318K

Temp	10% Ka	20% Ka	40% Ka	50% Ka	60% Ka	80% Ka
288K	0.56	0.70	1.20	1.28	1.40	0.93
298K	9.9	2.02	1.02	0.88	0.93	1.06
308K	0.17	0.31	0.53	0.44	0.43	0.31
318K	0.23	0.40	0.50	0.48	0.51	0.48

From Table 7 & 8 it has been found that at the same temperature, Ka value increases with increase in solvent proportions, but to some extent different in 40% to 60% in both (water + PC) and (water + THF) systems. As temperature increases, Ka value decreases normally. But some sort of discrepancies observed due to the switchover of ion-pair to ion-solvation interaction or vice versa.

According to the Fuoss, the slope of the plot $\log \lambda m$ vs $\log C$ is around -0.5, it is an indication of the presence of ion pairs in equilibrium.

From Table 2, succinic acid with (water + PC), the slope was found to be > -0.5. So, it suggests that there was an ion-pair present in equilibrium.

From the Table 3, succinic acid with (water + THF), the slope value was also found. -0.5. So here also observe ion-pair in equilibrium according to Fouss.

From Table 4, for both succinic acid with (water + PC) and (water + THF), as temperature increases, limiting molar conductance value increases. As the viscosity of THF is much lower than PC, so λ_m^{0} value increases with temperature. For this ion-solvent interaction process, activation of salvation is much important. The relation between limiting conductance value and activation solvation energy is related by this equation

$$\lambda m0 = A. e - \Delta Es/RT$$
 (ii)

Where A = pre exponential factor, ΔEs = activation salvation energy, R = Molar Gas constant,

Table 8: Ka (Association constant) values of succinic acid solvated in (Water +THF) medium from 288K to 318K

Temp	10%	20%	40%	50%	60%	80%
	Ka	Ka	Ka	Ka	Ka	Ka
288K	0.61	0.80	1.41	0.970	0.978	0.70
298K	0.47	0.75	0.85	0.92	1.0	0.76
308K	0.56	0.60	0.89	0.92	0.90	0.65
318K	0.48	0.80	1.26	0.97	0.86	0.83

T= Temperature in K.

If we plot $log\lambda_m^0$ vs 1/T, we get the slope. From the slope value we can easily calculate the activation salvation energy.

From the Table 5 and Table 6, show the value of Δ Es for succinic acid with (water + PC) and (water + THF) in different proportions.

 $\Delta Es = 10.54$ Kcals for succinic acid with (water + PC)< $\Delta Es = 12.57$ Kcals succinic acid with (water + THF). It indicate that the lower value of activation energy, higher the dissociation as well as higher possibility of ion-solvent interaction than ion-pair interaction.

From these two tables if we compare the dissociation constant value at different temperature for (water + PC) and (water + THF) medium, as temperature increases, Kc value increases. It is more increases for (water + PC) medium as dielectric constant is much more higher than THF medium.

The Gibbs energies of dissociation were calculated using the following equation

$$\Delta G = -RT \ln Kc$$
 (iii)

Where Kc= dissociation constant.

The enthalpy change (Δ H) of this dissociation process was calculated from the plot logKc vs 1/T. From the slope we can easily evaluate the value of Δ H. From the value of Δ G and Δ H, we can easily calculate ΔS for these systems by the equation

$$\Delta G = \Delta H - T \Delta S$$
 (iv)

Where $\Delta S = Entropy$ of solvation

Conductance value decreases with increase the percentage of PC as well as THF in water medium. This basic concept supports our result in our present experiment.



Fig. 1. Limiting conductance at 288K of succinic acid with (water + THF)



Fig. 2. Limiting conductance at 298K of succinic acid with (water + THF)



Fig. 3. Limiting conductance at 308K of succinic acid with (water + THF)



Fig.4. Limiting conductance at 318K of succinic acid with (water + THF)



Fig. 5. Limiting conductance at 288K of succinic acid with (water + PC)



Fig. 6. Limiting conductance at 298K of succinic acid with



Fig. 7. Limiting conductance at 288K of succinic acid with (water + PC)



Fig. 8. Limiting conductance at 318K of succinic acid with (water + PC)



Fig. 9. Plot of log λ m at infinite dilution with 1/T of succinic acid with (water + THF)





Fig. 20. Plot of log λ m vs logC of succinic acid with (water + THF) at 318K

Thermodynamic parameters were calculated with the help of Kc. ΔH value is negative for both the salvation processes. So it tells that in this dissociation process is exothermic in nature.

 ΔG value is much higher for (water + PC) medium which an indication of much spontaneous than (water + THF) medium.

 ΔS value is much negative for (water + PC) medium which indicate that this process is not much disorder for this ion solvent interaction process. At lower temperature, ΔS value is lower negative value. So, at lower temperature, ion solvent interaction is much random.

Figure 1 to Fig. 4 shows the plot of shows the plot $1/\lambda m$ vs. λmC of Succinic acid with (water+THF) medium.

Figure 5 to Fig. 8 shows the plot of shows the plot $1/\lambda m$ vs. λmC of Succinic acid with (water+PC) medium.

From these above plots we can evaluate $\lambda_m{}^{_0}$ and Kc from the the slope and intercept respectively.

Figure 9. shows $log\lambda m$ at infinite dilution with 1/T of succinic acid with (water + THF). From this graph we can evaluate the activation salvation energy with the help of slope. Fig.10. shows the Plot of logKc with 1/T of succinic acid with (water + THF). From the slope we can calculate the ΔH for this system.

Figure 11. shows the Plot of log λ m at infinite dilution with 1/T of succinic acid with (water + PC).

From this graph we can evaluate the activation salvation energy with the help of slope. Fig. 12. shows the Plot of logKc with 1/T of succinic acid with (water + PC). From the slope we can calculate the ΔH for this system.

Figure 13. to Fig. 16 show the Plot of $\log \lambda m$ vs logC of succinic acid with (water + PC) at 288K to 318K. From these plots we evaluate the slope. From the slope value we imagine that at equilibrium the systems are ion-pair interaction occurs or not.

Figure 13. to Fig.16 show the Plot of $\log\lambda m$ vs $\log C$ of succinic acid with (water + THF) at 288K to 318K. From these plots we evaluate the slope. From the slope value we imagine that at equilibrium the systems are ion-pair interaction occurs or not.

From these 8 plots it has been found that both systems show ion-pair interaction in equilibrium processes according to Fuoss.

For the further studies in this way we can easily calculate the thermodynamic parameters in different solutions in different concentrations (where different types of interaction happened). So, solution chemistry reveals of different ideas in physical chemistry.

CONCLUSION

From the solavation study of succinic acid with (water + PC) and (water + THF) medium it has been found that with increase in temperature limiting molar conductace increases in both the systems. Degree of dissociation (Kc) increases in both PC and THF medium. But it has been noted that to some extent high for PC medium. This is due to the high dielectric constant value of this medium. In both cases Δ H value is negative. So, these ion-solvent interaction systems are exothermic in nature. Δ G value is much higher for (water + PC) medium which an indication of much spontaneous than (water + THF) medium. Δ S value is much negative for (water + PC) medium which indicate that this process is not much disorder for this ion solvent interaction process. $\Delta Es = 10.54$ Kcals for succinic acid with (water + PC)< $\Delta Es = 12.57$ Kcals succinic acid with (water + THF). It indicate that the lower value of activation energy, higher the dissociation as well as higher possibility of ion-solvent interaction than ion-pair interaction.

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