Searching for ion-solvent interaction of AcOH with (water + AN) and (water + DMF) medium in different temperatures

Subhasish Nayak[1], Piru Hens[2] and Ashoke Hazra*[3]

[3] Dept. of Chemistry, A.K.P.C. Mahavidyalaya, Bengai, Hooghly-712611, W.B.

[1,2] M.Sc, Dept. of Chemistry, Bankura University, W.B.

Abstract

Present work describes how weak electrolyte solvated in aqueous and non-aqueous mix solvent systems. For this study conductance and thermodynamic techniques were used. Limiting molar conductance was measured by using Karus-Bray equation. It was verified by Shedlovsky method. During ion-solvent interaction study, ion-pair formation was verified by Fuoss equation. All the experiments were performed in AcOH with (water+DMF) and (water+AN) medium in different proportions in different temperatures. It was found that with increase in temperature limiting molar conductance increases, as well as association constant increases and also dissociation constant decreases which support our basic assumption for ion solvent interaction study. For AcOH with (water+DMF), at 60% and 80% Ka value was much higher than that of other proportions. For AcOH with (water+AN), at 80% Ka value was increases than the other proportions. Thermodynamic data supports our ion-solvent interaction study. Negative value of ΔG indicated the spontaneity of this study.

Keyword: AcOH, AN, DMF, Conductance, solvation.

Introduction

In continuation our earlier studies [1-3] we have seen that PC and THF act as good co-solvent for ion-solvent interaction studies. Solvent polarity on the acid dissociation constants of weak acids has also been studied [4-10].

Conductance measurements can be used to determine solvent polarity, dissociation constant and association constant of acids [11-16].

Acetic acid is an antibiotic that treats infections caused by a bacteria or fungus. It is an important chemical reagent for laboratory and industrial chemical used primarily in the production of cellulose acetate for photographic film, polyvinyl acetate for wood glue and synthetic fibres etc.[17].

In the present study we used DMF and AN as non-aqueous solvent with water for the ion-solvent interaction of AcOH with different proportions i.e, 10%, 20%, 40%, 50%, 60% and 80% of solvents in different temperatures i.e, 288K, 298K, 308K and 318K.

Experimental

Materials

Acetic acid (Loba Chemie, India), DMF (LOBA Chemicals), AN (LOBA Chemicals) were used as such, without any further purification.

Solutions Preparation

The solution of Acetic Acid in water and different compositions (10%, 20%, 40%, 50%, 60%, 80%) of DMF and AN were prepared. Acetic Acid solution (0.1M) was prepared in conductivity water, water +DMF and water +AN in volume ratio (v/v).

Conductivity Study

Conductivity of the above solutions was 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 Discussions

Molar conductance data was observed in different composition of acetic acid solution with (water+DMF) and (water+AN). As acetic acid is weak electrolyte, to determine limiting molar conductance was not measured by Onsagar equation. To determine limiting molar conductance we use Karus-Bray [18] conductivity equation.

The equation is $1/\lambda m = 1//\lambda m^0 + \lambda mC/ (\lambda_m{}^{02}Kc)$.....(i)

Where Kc =dissociation constant, C = conc. in mol/ dm^3, λm^0= molar conductance at infinite dilution.

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

We used Shedlovsky equation [19] to evaluate the absolute limiting molar conductance.

$1/S\lambda m = 1/\lambda_m{}^0 + C\lambda mSf\pm^2Ka/\lambda_m{}^{02}$.....(ii)

Table1: Physical Parameters of AN (Acetonitrile) and DMF(Dimethyl Formamide)

Solvents	Viscosity	Solubility parameters	Surface tension	Dielectric constant
AN	0.344	22.5	26.64	36.04
DMF	0.802	24.9	35.20	36.71

Table 1 shows the physical parameters of DMF(Dimethyl Formamide) and AN(Acetonitrile) solvents.

Table2: Limiting Molar conductance, Dissociation Constant(Kc) and Solvation Activation Energy of AcOH in (water+DMF) and (water+AN) medium

Temp	AcOH+DMF			AcOH+AN		
	λm^0	Kc	Es	λm^0	Kc	Es
288K	0.169	0.665		0.161	0.667	
298K	0.198	0.490	6.038KCal	0.185	0.515	5.646KCal
308K	0.290	0.231		0.262	0.267	
318K	0.411	0.169		0.369	0.175	

From the Table 2, it has been found that with it has been found that with increase in temperature, limiting conductance value increases both the systems. But in case of AcOH with (water + DMF) , λ_m^0 is to some extent high than that of AcOH with (water + AN). This is due to the high dielectric constant value of the DMF solvent.

Dissociation constant (Kc) value decreases with increase in temperature for both these systems. But in case of AcOH with (water + DMF), Kc value was to some extent less than that of AcOH with (water + AN). This indicates that the solvation process increases in DMF medium. From the activation solvation energy data, it was observed that both systems, solvation activation energy more or less same ≈ 6 KCals.

Table3: Association Constant value of AcOH in (water+DMF) in different proportion in different temperatures

Temperature	% of DMF(Dimethyl Formamide) in AcOH solution					
	10%	20%	40%	50%	60%	80%
288K	1.89	1.80	1.26	1.22	1.38	1.75
298K	2.07	3.06	2.06	1.86	2.08	2.09
308K	3.61	6.24	3.71	4.51	4.8	4.38
318K	6.51	7.43	3.94	5.10	7.15	7.13

Table 3 shows the association constant (Ka) data of AcOH with (water + DMF) in different proportions i.e, 10%, 20%, 40%, 50%, 60%, 80% in different temperatures. It was observed that with increase in temperature association constant increases, i.e, dissociation constant (Kc) value decreases, which was supported from Karus-Bray equation [18]. Association constant values were calculated from the α(degree of association) value, limiting conductance value, and the relation

$Ka = (1-\alpha)/\alpha^2C$.....(iii)

It was observed that at 80% DMF with AcOH solution, Association constant value was higher at higher temperature.

We evaluate λ_m^0 from Karus-Bray equation. Parallely we cross checking the value of λ_m^0 from Shedlovsky. λ_m^0 value is more or less same for these two methods.

Table4: Association Constant value of AcOH in (water+AN) in different proportion in different temperatures

Temperature	% of AN(Acetonitrile) in AcOH solution					
	10%	20%	40%	50%	60%	80%
288K	1.89	1.93	1.18	1.15	1.153	2.21
298K	2.07	3.06	1.83	1.86	1.64	2.35
308K	2.46	4.94	2.94	4.24	4.52	3.85
318K	4.74	6.61	4.18	4.51	5.84	7.69

Table 4 shows the Ka value of AcOH with (water + AN) medium. With increase in temperature, Ka value increases. For this system at 80% AN(Acetonitrile) with AcOH solution, Ka value is too much high other than 20% to 60%.

Table5: Thermodynamic parameters of AcOH in (water+DMF) medium in different proportions in different temperatures

Percentage of DMF in AcOH	Thermodynamic parameters (in Cals)	Temperature			
		288K	**298K**	**308K**	**318K**
10%	ΔG	-363	-429	-785	1183
	ΔS	-5.17	-4.77	-3.46	-2.10
	ΔH	**-1853**			
20%	ΔG	-336	-661	-1120	-1266
	ΔS	-6.31	-5.01	-3.36	-2.79
	ΔH	**-2155**			
40%	ΔG	-131	-429	-801	-865
	ΔS	-5.58	-4.39	-4.25	-2.74
	ΔH	**-1739**			
50%	ΔG	-113	-366	-921	-1028
	ΔS	-7.41	-6.31	-4.30	-3.83
	ΔH	**-2248**			
60%	ΔG	-183	-433	-959	-1242
	ΔS	-8.07	-6.96	-5.02	-3.98
	ΔH	**-2508**			
80%	ΔG	-320	-436	-903	-1241
	ΔS	-6.35	-5.75	-4.05	-2.86
	ΔH	**-2151**			

Table 5 shows the thermodynamic parameters of AcOH with (water+DMF) medium. ΔH values were calculated from logKa vs. 1/T plot. Negative value of ΔH confirmed that the ion-solvent interaction process was exothermic. The negative value of ΔG indicated that the solvation process was spontaneous in nature. ΔS value was calculated with the help of ΔG and ΔH values. With increase in temperature, lower negative values of ΔS observed. Negative value of ΔS always indicated that these ion-solvent interaction process was entrophically non favourable.

For every proportions of DMF(Dimethyl Formamide), it was observed that ΔG value increases with increase in temperature which was negative. So, systems were highly spontaneous. At lower temperature, entrophically less favourable than that of high temperature. 20%, 60%, 80% of DMF solvents are more ion-solvent interaction favourable according to ΔG value. 10%, 20%, 40% and 80% are entrophically more favourable for ion-solvent interaction. More negative value of ΔH value was observed in 60% solution which was exothermic in nature. From the above findings it was expected that 60% DMF solvent with AcOH was more favourable for ion-solvent interaction supported by the thermodynamic parameters such as ΔG, ΔS and ΔH values.

Table6: Thermodynamic parameters of AcOH in (water+AN) medium in different proportions in different temperatures

Percentage of AN in AcOH	Thermodynamic parameters (in Cals)	Temperature			
		288K	**298K**	**308K**	**318K**
10%	ΔG	-363	-429	-549	-982
	ΔS	-3.15	-2.82	-2.34	-0.91
	ΔH	**-1272**			
20%	ΔG	-375	-661	-976	-1193
	ΔS	-4.99	-3.86	-2.71	-1.94
	ΔH	**-1813**			
40%	ΔG	-93	-357	-659	-903
	ΔS	-6.11	-5.03	-3.88	-2.99
	ΔH	**-1856**			
50%	ΔG	-79	-366	-883	-947
	ΔS	-7.12	-5.92	-4.05	-3.72
	ΔH	**-2131**			
60%	ΔG	-80	-291	-923	-1114
	ΔS	-8.59	-7.60	-5.30	-4.53
	ΔH	**-2556**			
80%	ΔG	-453	-505	-824	-1287
	ΔS	-4.80	-4.46	-3.28	-1.72
	ΔH	**-1837**			

Table 6 shows that the thermodynamic parameters of different proportions of AcOH with (water +AN) in different temperatures. Negative value of ΔH supported that the ion-solvent interaction study was exothermic in nature and also supported our basic concept of ion-solvent interaction study. All these proportions ΔG values were negative which means that these ion-solvent interaction processes are spontaneous. From Table 5 it was also observed that ΔG value was more decreased in 20%, 60% and 80%. ΔH value was more negative in 60%. From the above findings it was concluded that 20%, 60% and 80% proportions were to some extent more favourable for ion-solvent interaction studies.

For AcOH with (water+DMF), we plotted logλm vs. logC in different proportions in different temperatures it was observed that slope value was greater than '-5'. It was indicated that for

this ion-solvent interaction study, ion-pair formed in equilibrium condition according to Fuoss equation [20].

Similar result was observed when we plot logλm vs. logC in different proportions in different temperatures for AcOH with (water +AN) medium. Here also ion-pair formed in equilibrium condition.

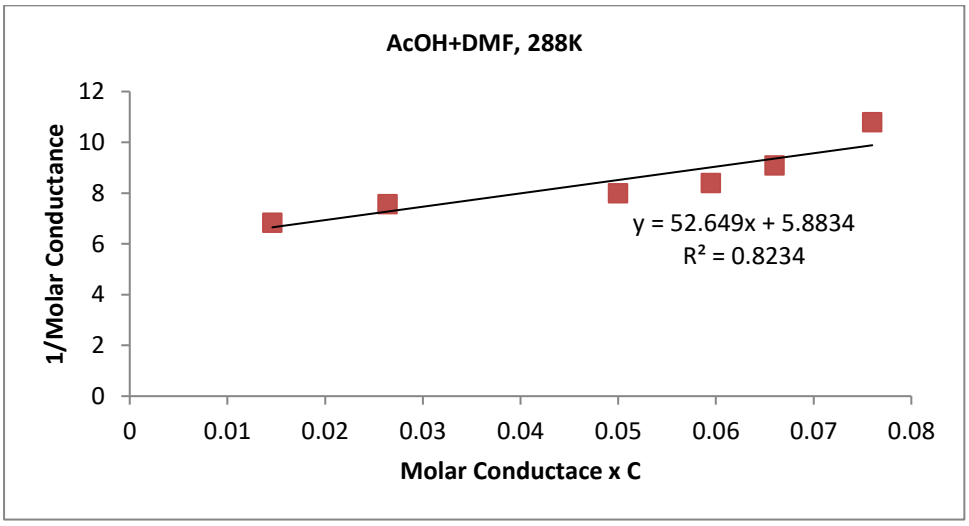

Fig.1. Limiting conductance at 288K of Acetic acid with (water + DMF)

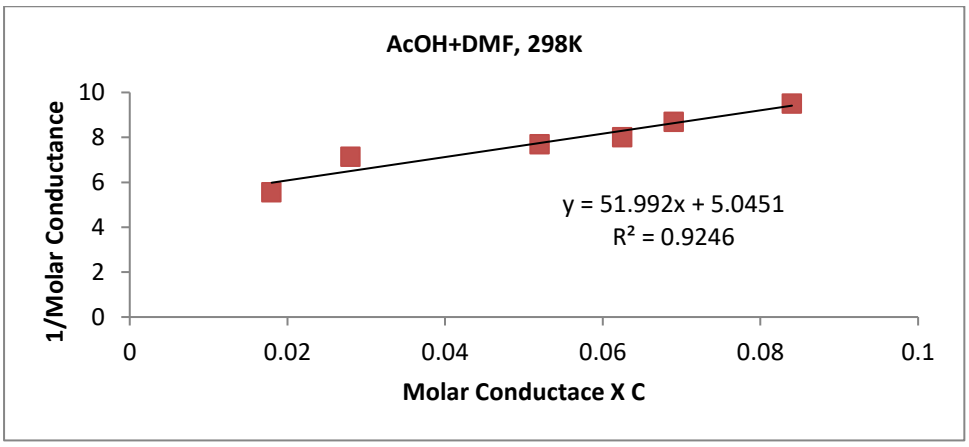

Fig.2. Limiting conductance at 298K of Acetic acid with (water + DMF)

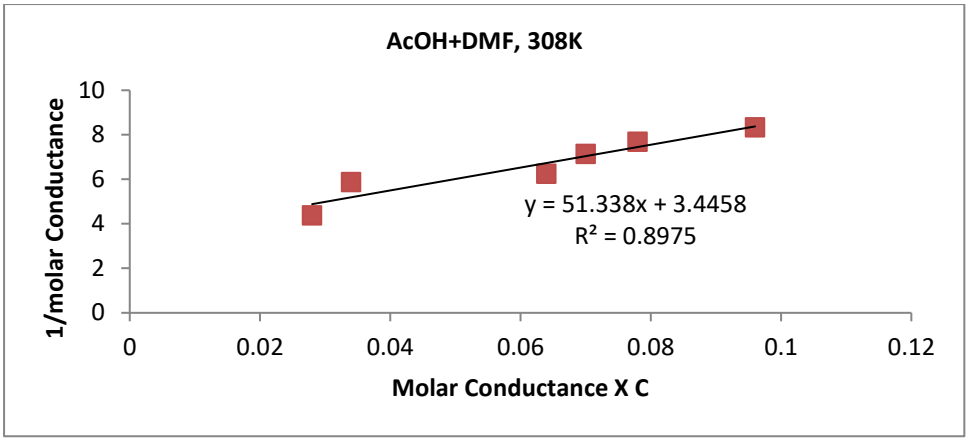

Fig.3. Limiting conductance at 308K of Acetic acid with (water + DMF)

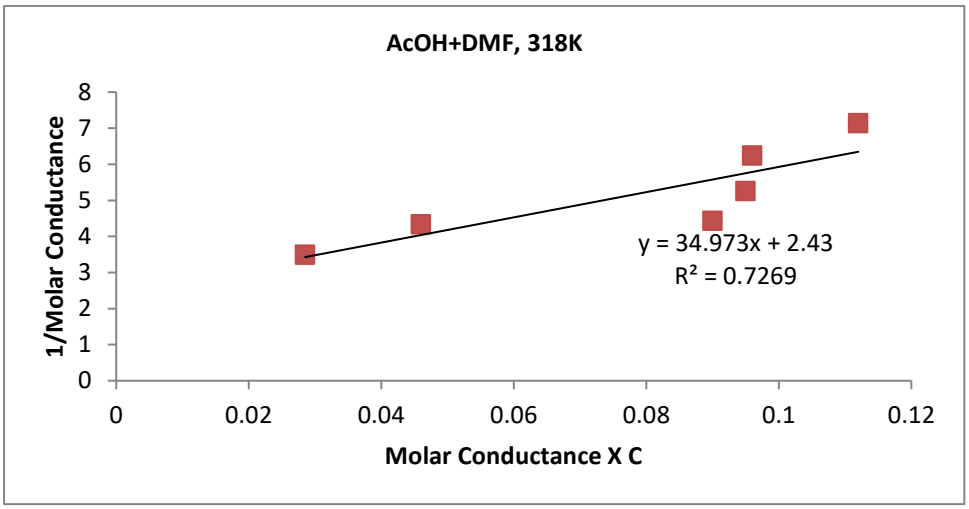

Fig.4. Limiting conductance at 318K of Acetic acid with (water + DMF)

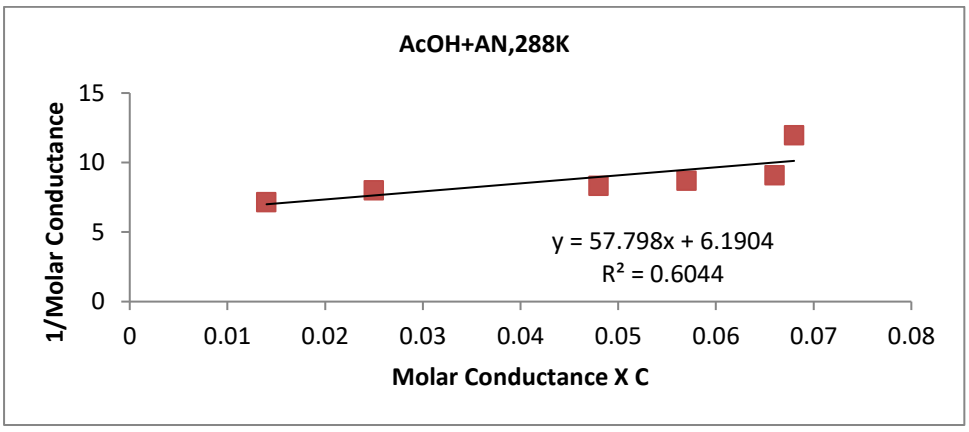

Fig.5. Limiting conductance at 288K of Acetic acid with (water + AN)

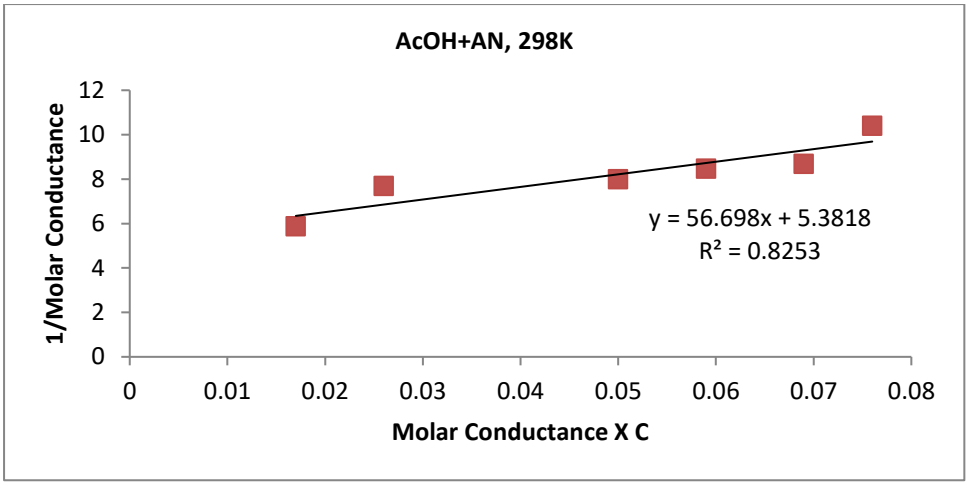

Fig.6. Limiting conductance at 298K of Acetic acid with (water + AN)

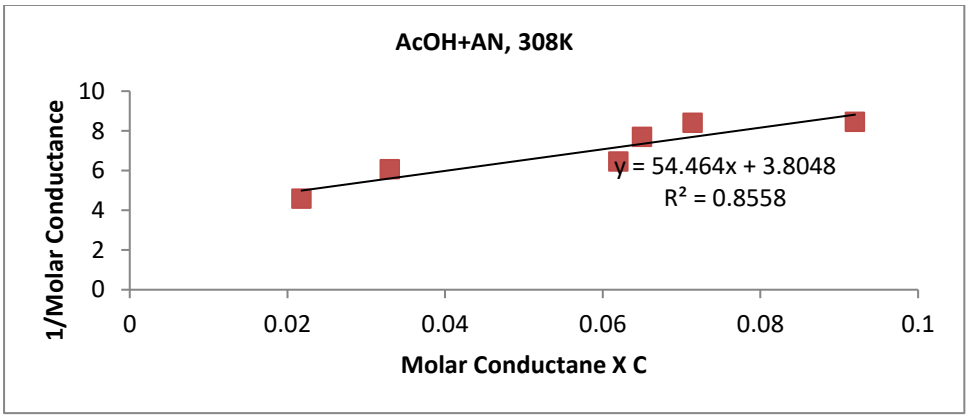

Fig.7. Limiting conductance at 308K of Acetic acid with (water + AN)

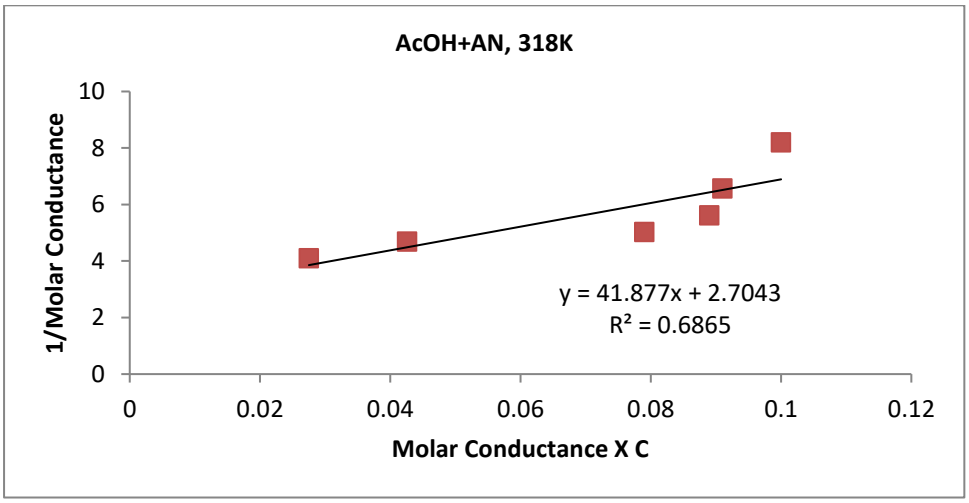

Fig.8. Limiting conductance at 318K of Acetic acid with (water + AN)

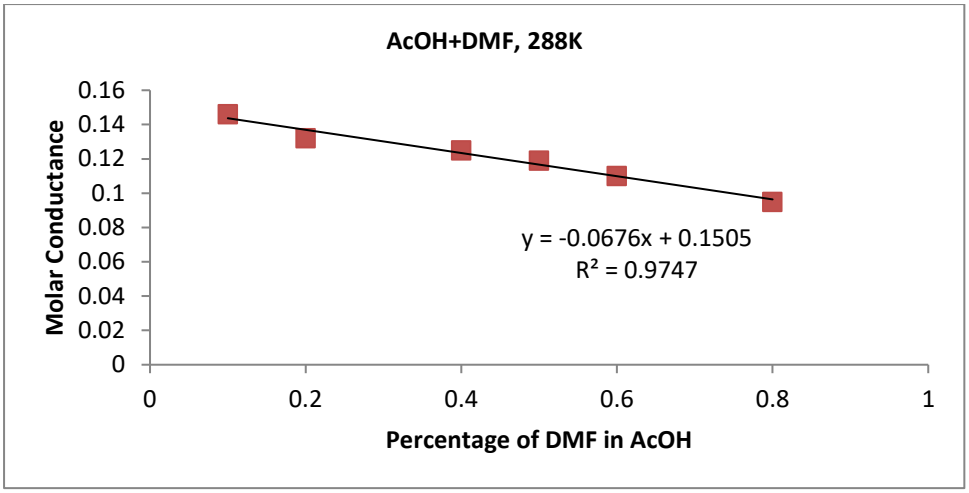

Fig.9. Molar Conductance vs. Percentage of DMF in AcOH plot at 288K

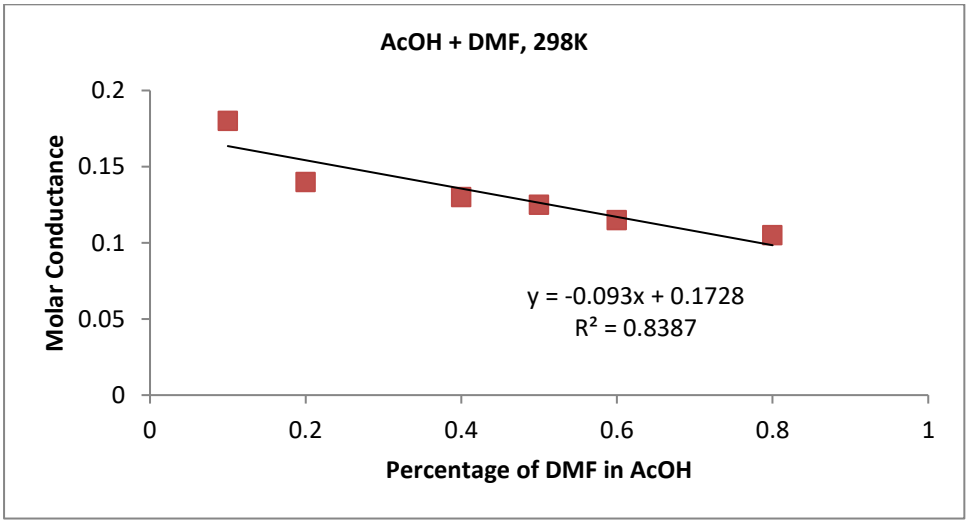

Fig.10. Molar Conductance vs. Percentage of DMF in AcOH plot at 298K

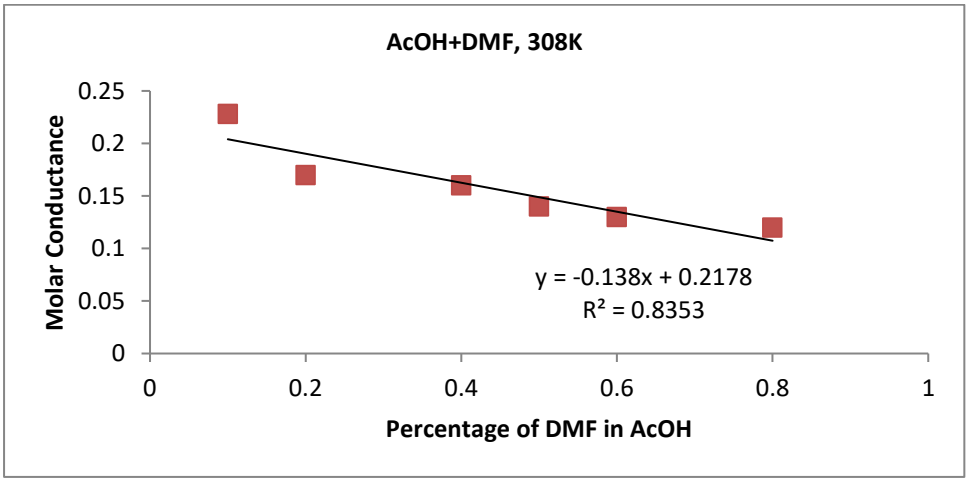

Fig.11. Molar Conductance vs. Percentage of DMF in AcOH plot at 308K

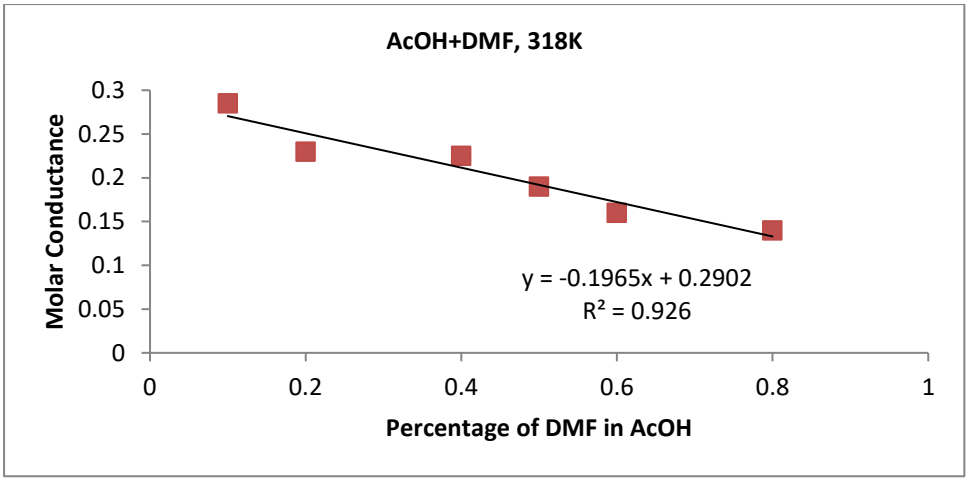

Fig.12. Molar Conductance vs. Percentage of DMF in AcOH plot at 318K

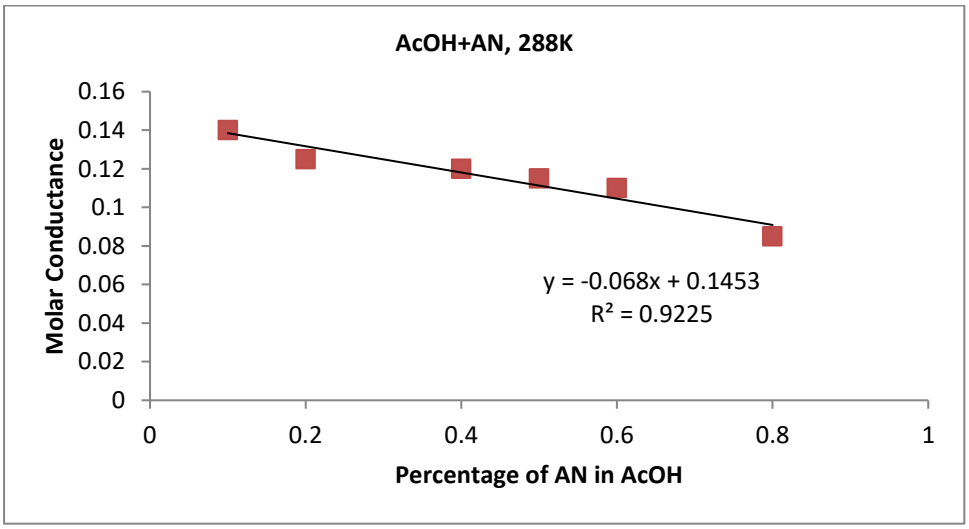

Fig.13. Molar Conductance vs. Percentage of AN in AcOH plot at 288K

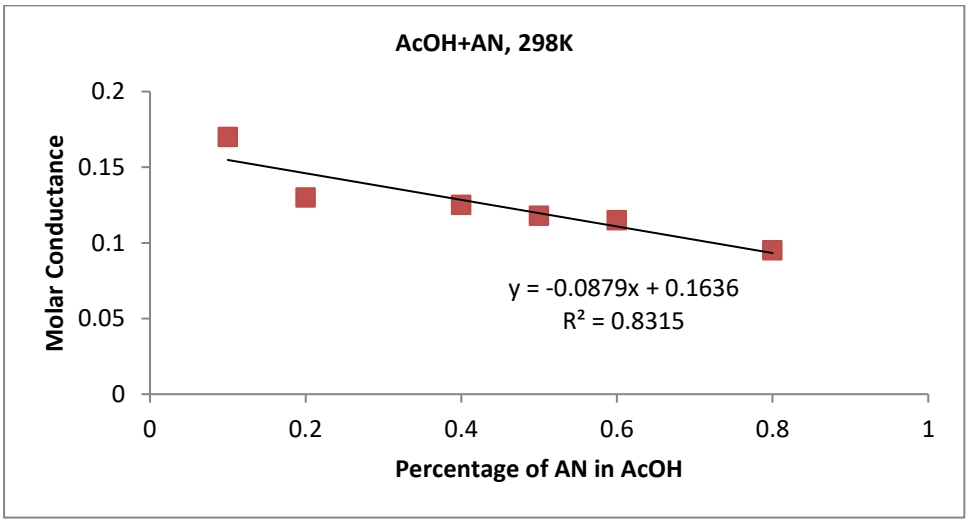

Fig.14. Molar Conductance vs. Percentage of AN in AcOH plot at 298K

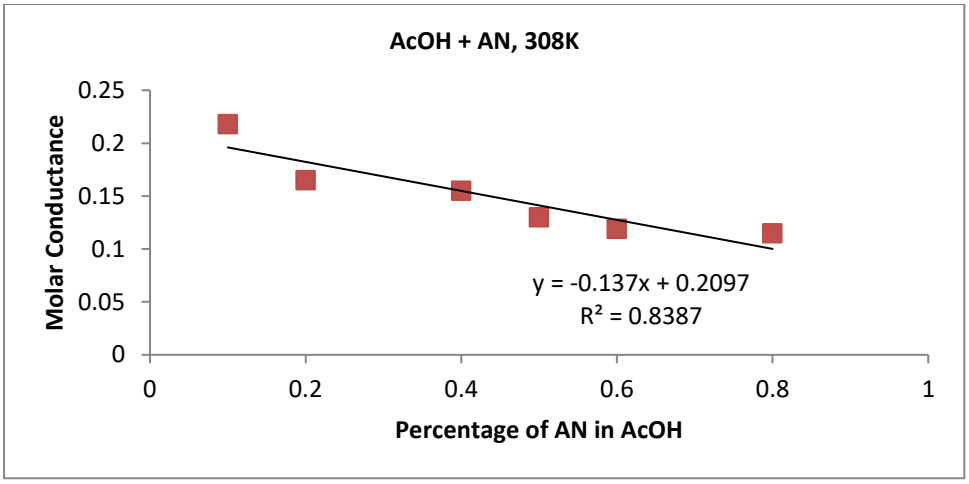

Fig.15. Molar Conductance vs. Percentage of AN in AcOH plot at 308K

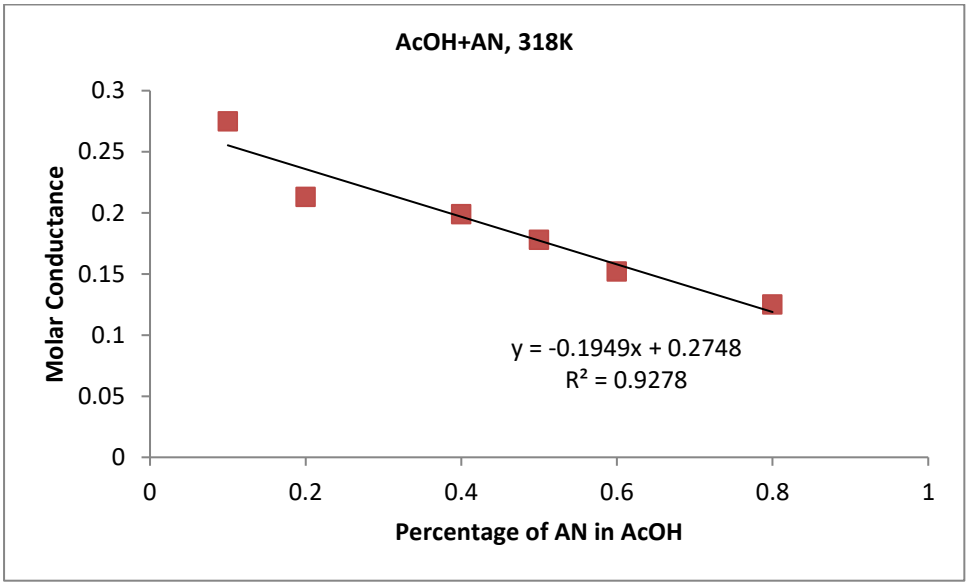

Fig.16. Molar Conductance vs. Percentage of AN in AcOH plot at 318K

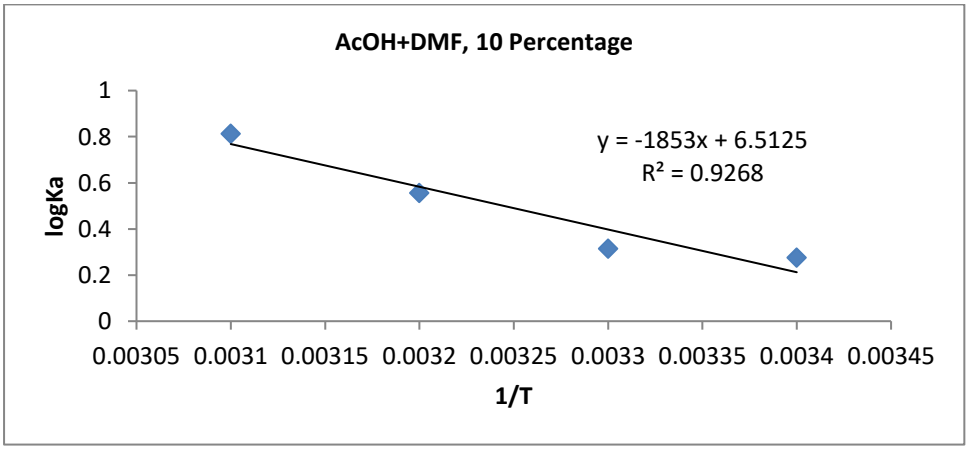

Fig.17. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 10%

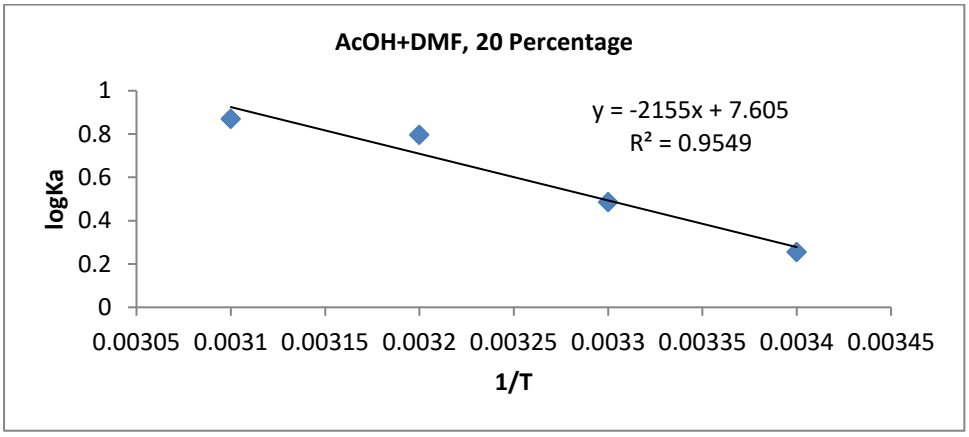

Fig.18. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 20%

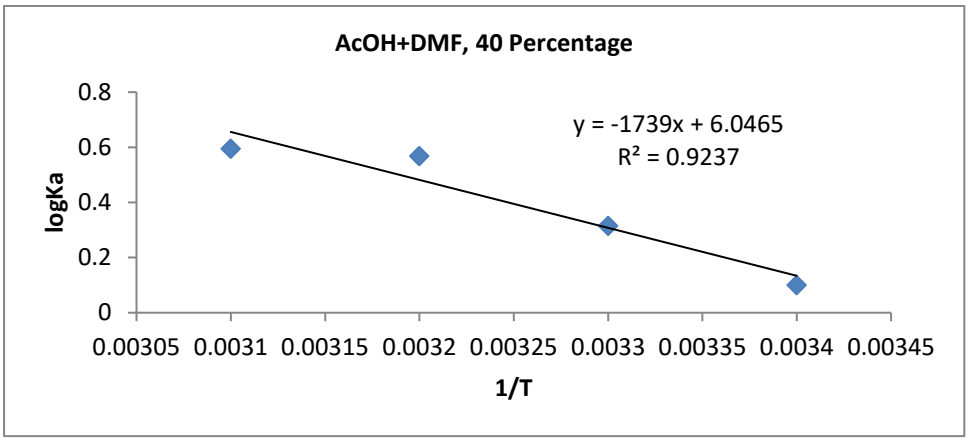

Fig.19. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 40%

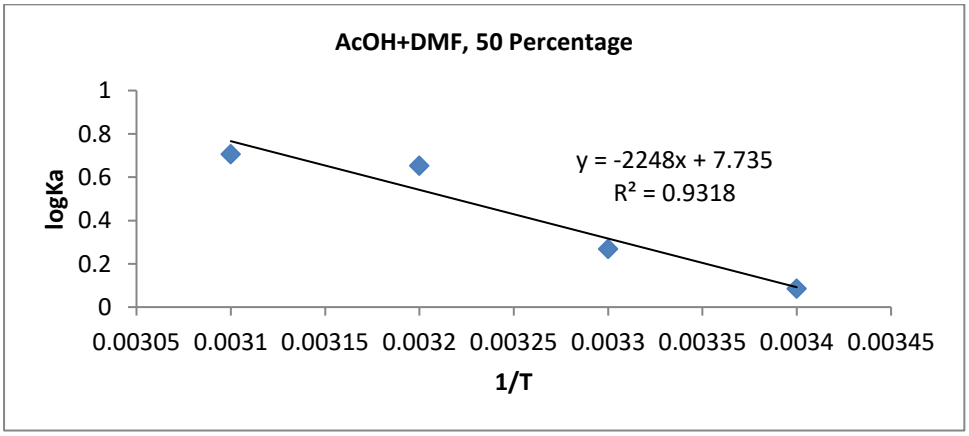

Fig.20. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 50%

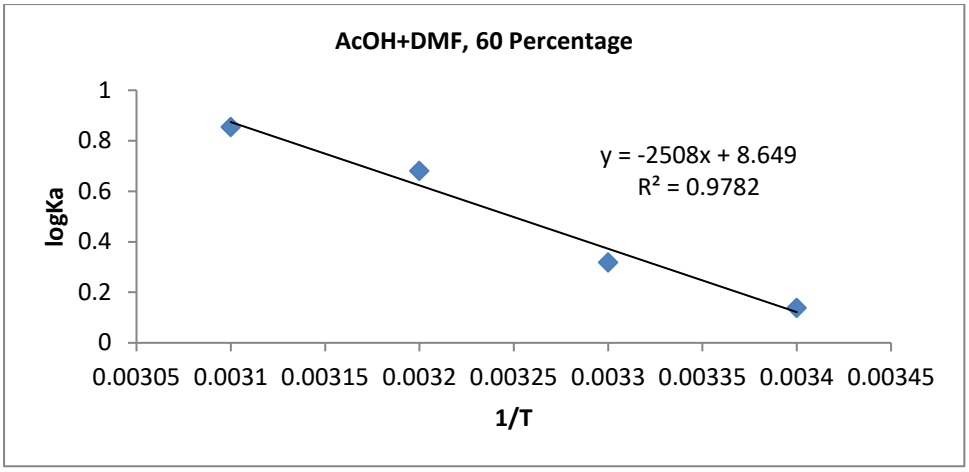

Fig.21. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 60%

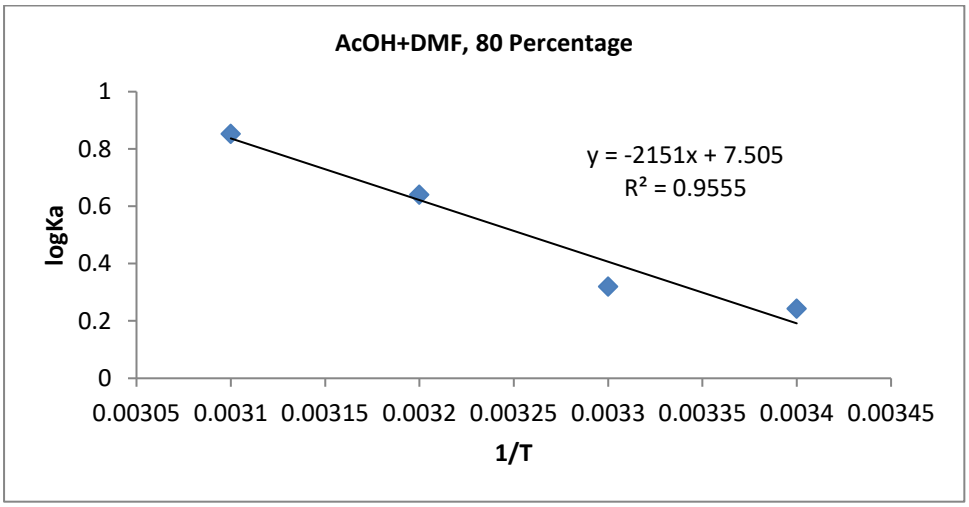

Fig.22. Plot of logKa with 1/T of Acetic acid with (water + DMF) at 80%

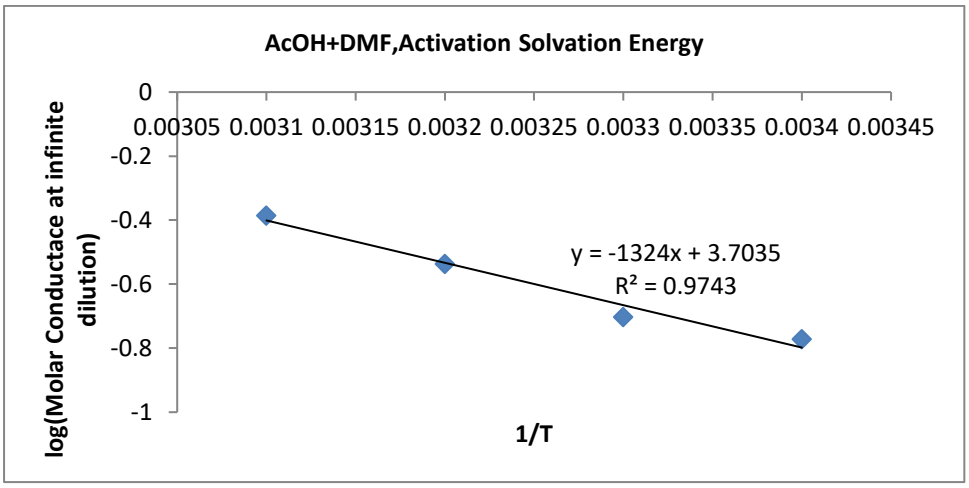

Fig.23. Plot of logλm at infinite dilution with 1/T of Acetic acid with (water + DMF)

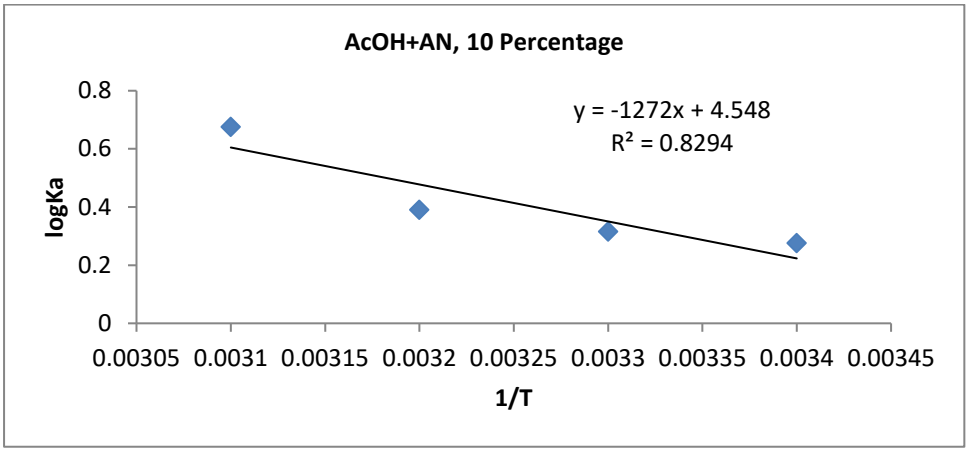

Fig.24. Plot of logKa with 1/T of Acetic acid with (water + AN) at 10%

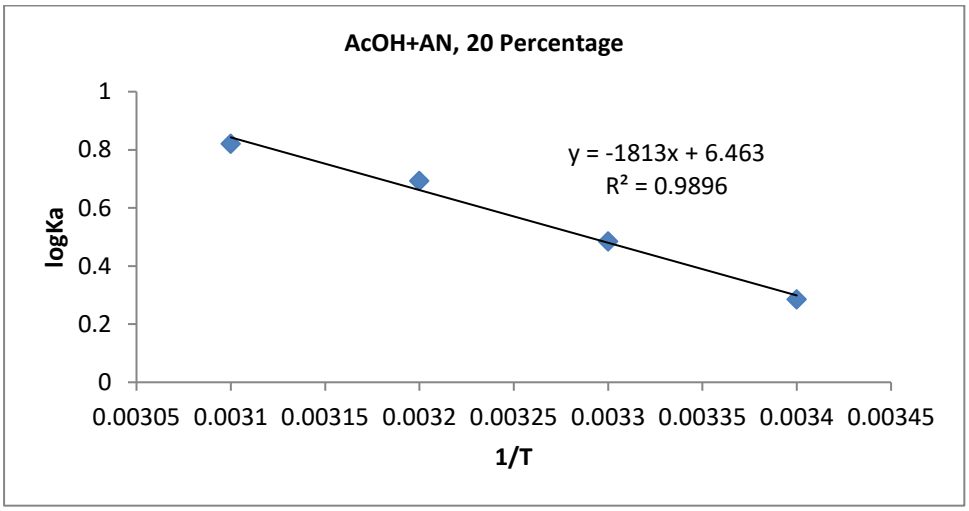

Fig.25. Plot of logKa with 1/T of Acetic acid with (water + AN) at 20%

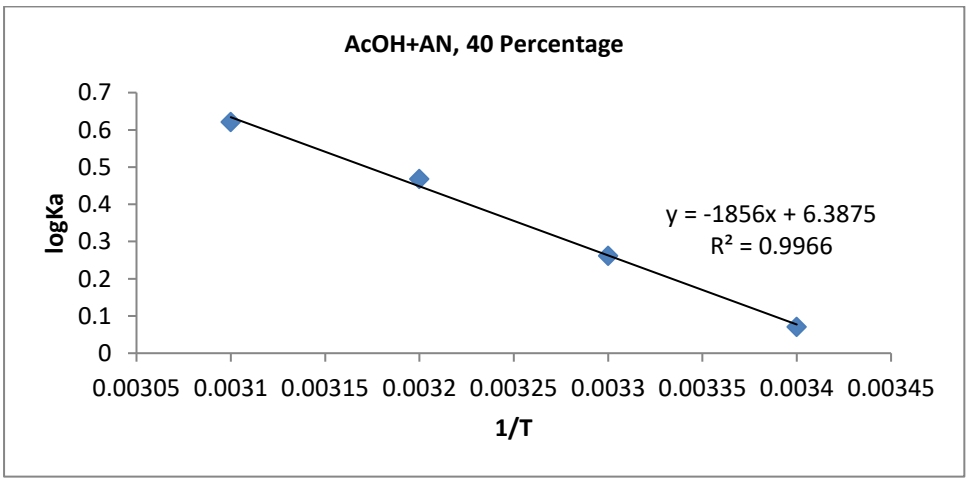

Fig.26. Plot of logKa with 1/T of Acetic acid with (water + AN) at 40%

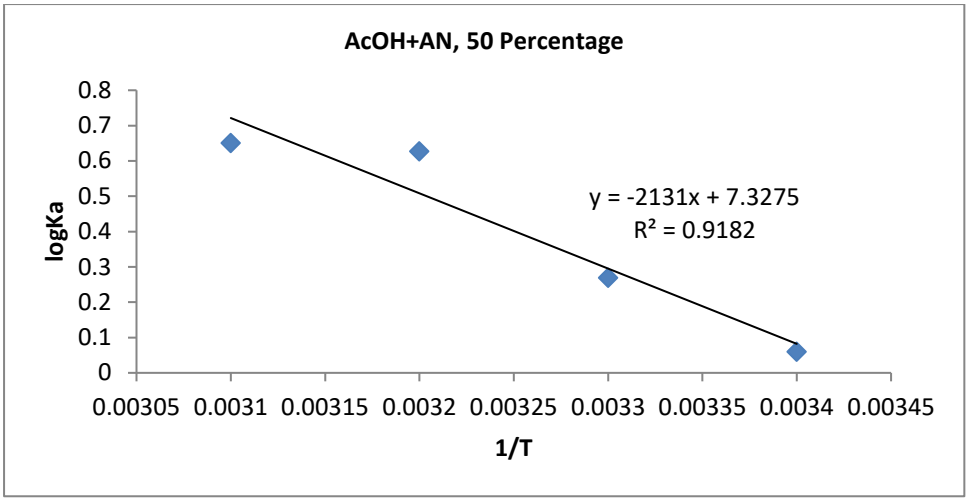

Fig.27. Plot of logKa with 1/T of Acetic acid with (water + AN) at 50%

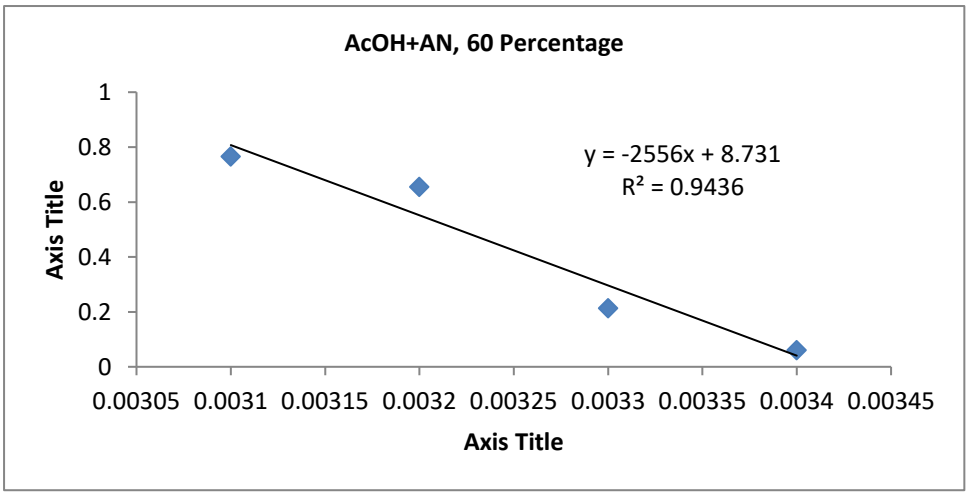

Fig.28. Plot of logKa with 1/T of Acetic acid with (water + AN) at 60%

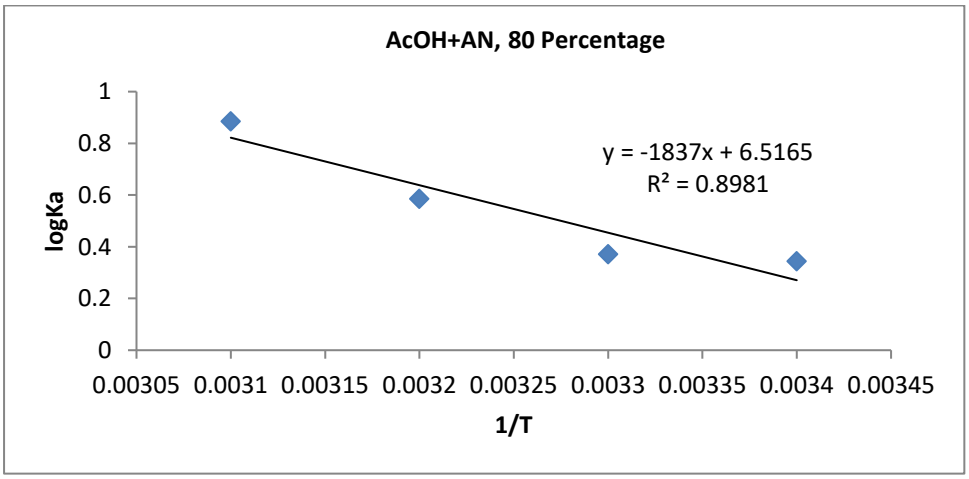

Fig.29. Plot of logKa with 1/T of Acetic acid with (water + AN) at 80%

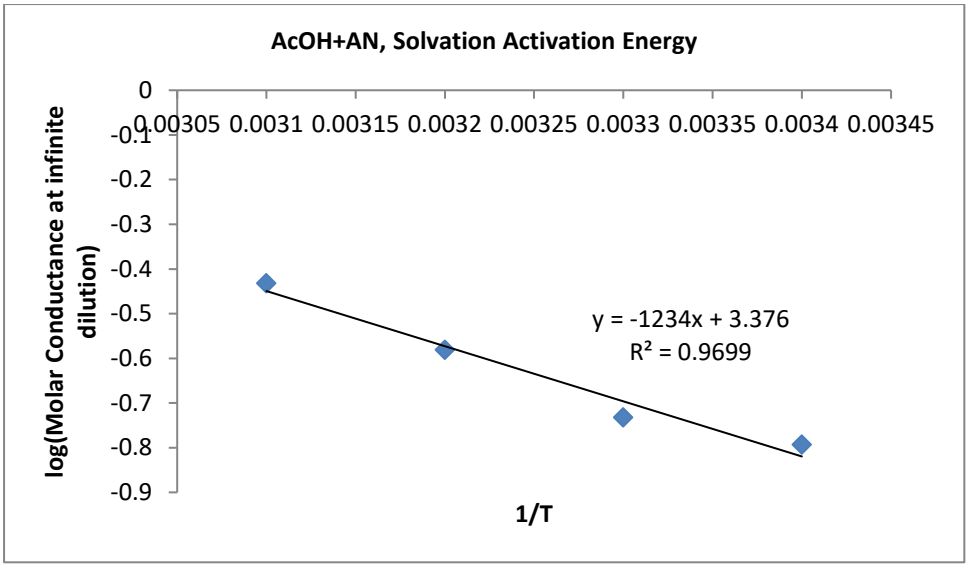

Fig.30. Plot of logλm at infinite dilution with 1/T of Acetic acid with (water + AN)

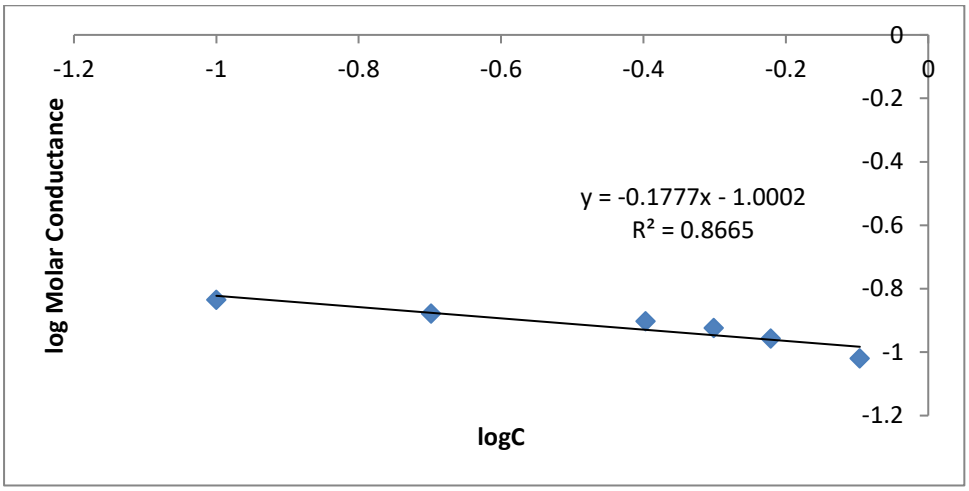

Fig.31. Plot of log Molar Conductance vs log C at 288K of Acetic acid with (water + DMF)

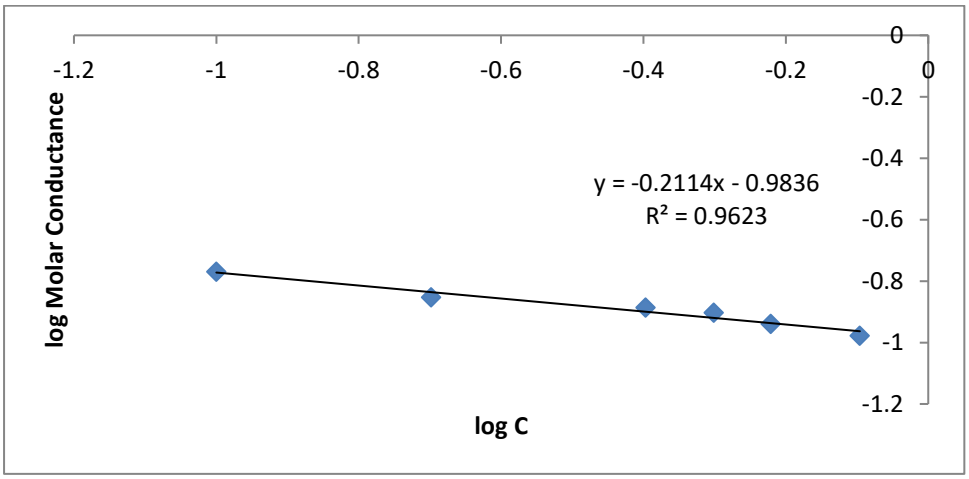

Fig.32. Plot of log Molar Conductance vs log C at 298K of Acetic acid with (water + DMF)

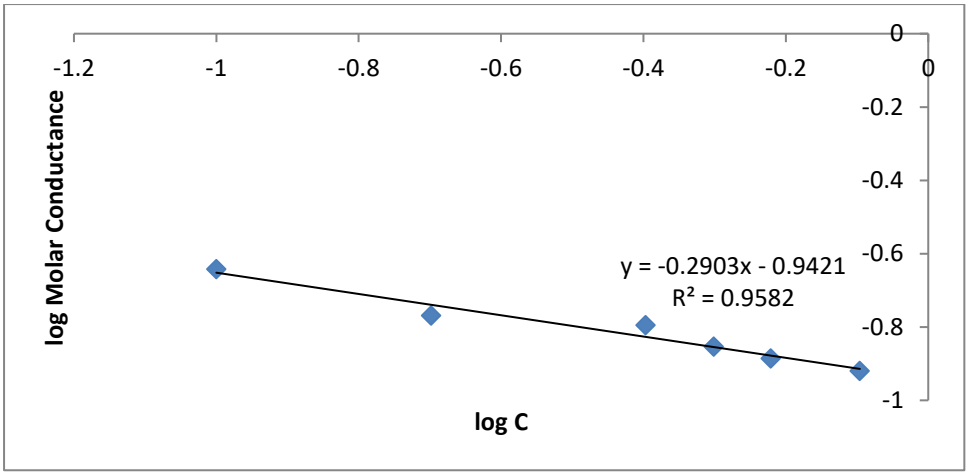

Fig.33. Plot of log Molar Conductance vs log C at 308K of Acetic acid with (water + DMF)

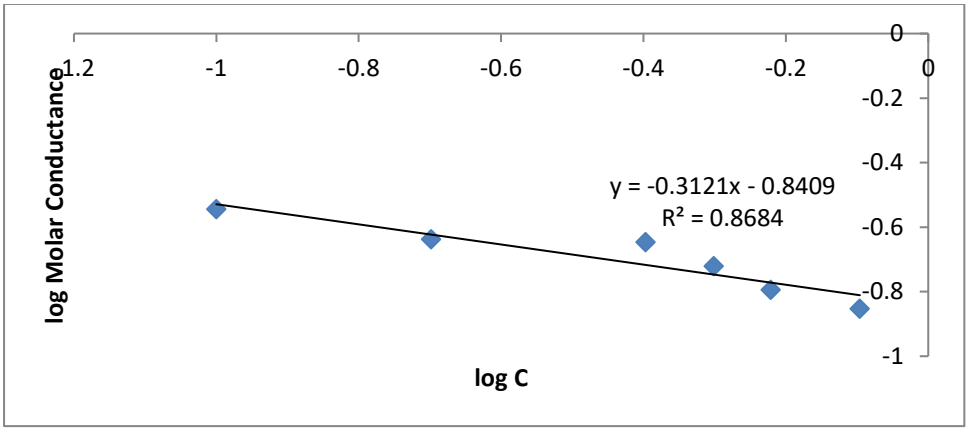

Fig.34. Plot of log Molar Conductance vs log C at 318K of Acetic acid with (water + DMF)

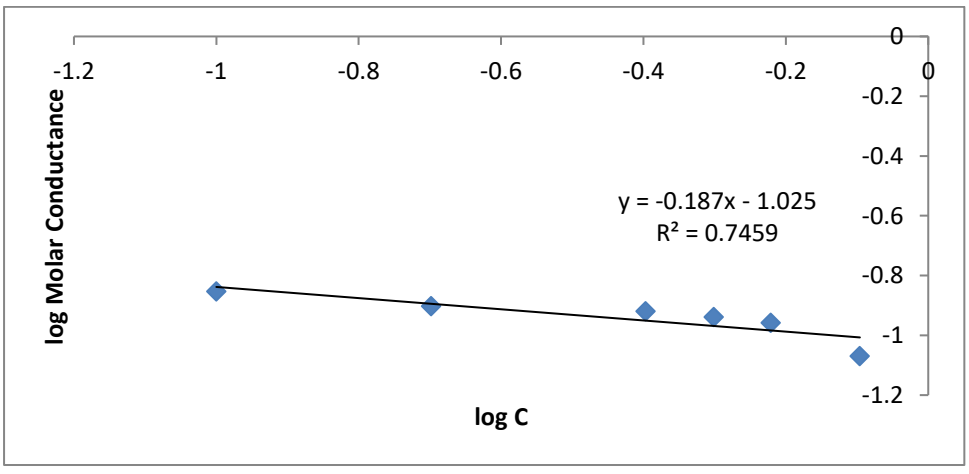

Fig.35. Plot of log Molar Conductance vs log C at 288K of Acetic acid with (water + AN)

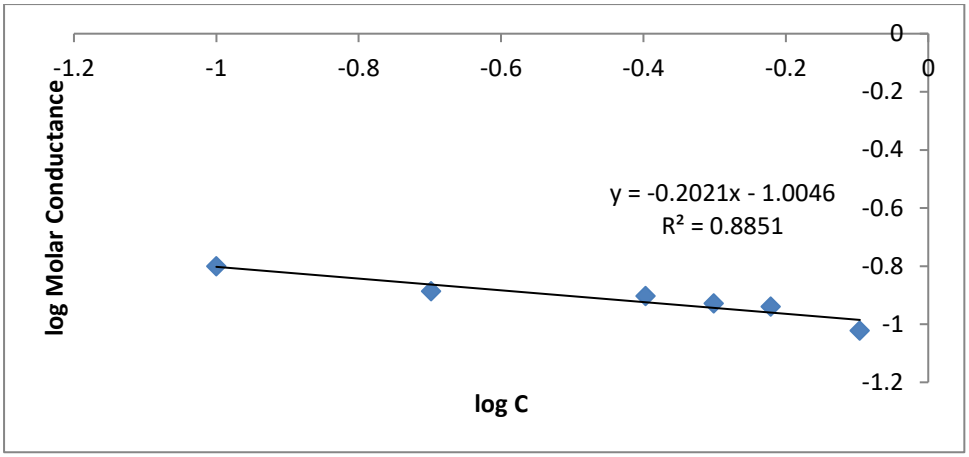

Fig.36. Plot of log Molar Conductance vs log C at 298K of Acetic acid with (water + AN)

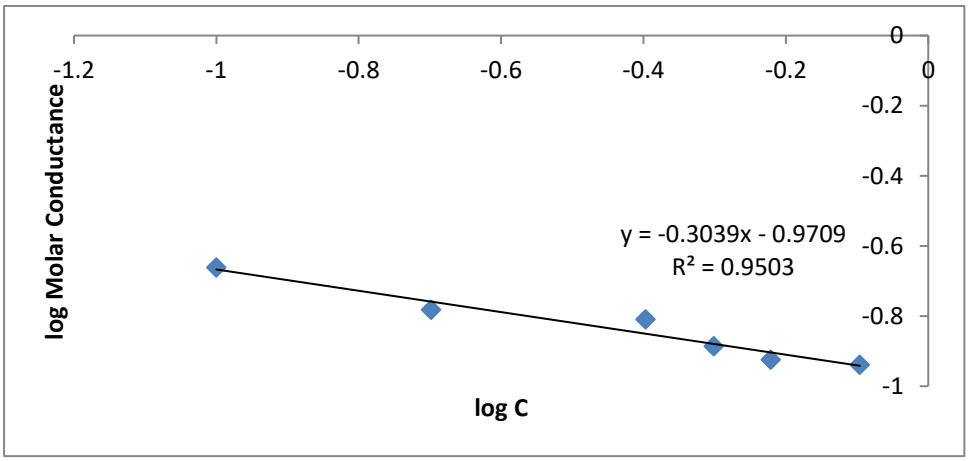

Fig.37. Plot of log Molar Conductance vs log C at 308K of Acetic acid with (water + AN)

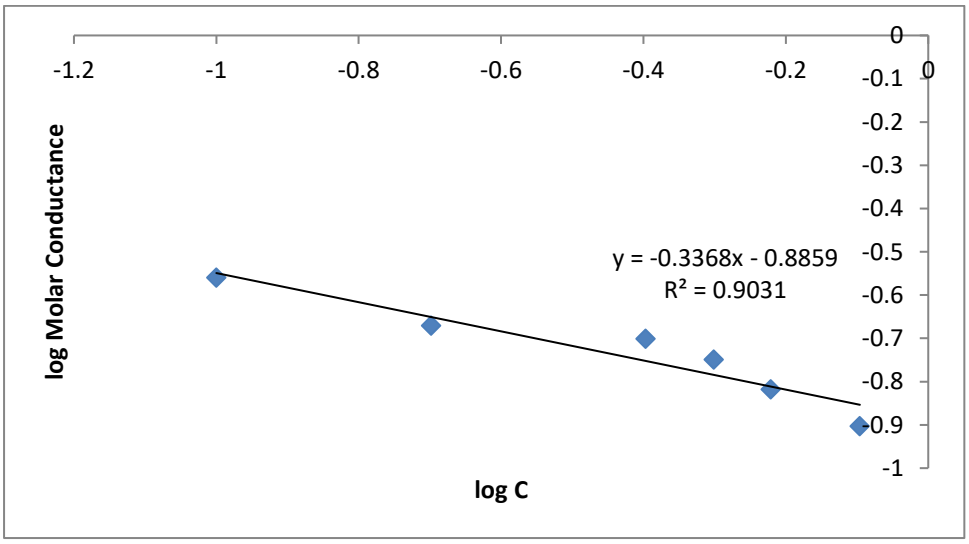

Fig.38. Plot of log Molar Conductance vs log C at 318K of Acetic acid with (water + AN)

Fig1 to Fig4 show Karus-Bray curve to determination of limiting molar conductance and dissociation constant of AcOH with (water +DMF) solvent media in different temperatures.

Fig5 to Fig8 shows Karus-Bray curve to determination of limiting molar conductance and dissociation constant of AcOH with (water +AN) solvent media in different temperatures.

Fig 9 to Fig 12 shows the Molar conductance vs Percentage of DMF in AcOH in different temperatures. Figs 13 to Fig 16 show the Molar conductance vs Percentage of AN in AcOH in different temperatures. Here normal tendency was observed from these plots.

Fig 17 to Fig 22 shows Plot of logKa with 1/T of Acetic acid with (water + DMF) at 10%, 20%, 40%, 50%, 60% & 80% proportions in different temperatures. These plots help us to calculate the change in enthalpy for these solvation processes.

Fig 23 shows Plot of logλm at infinite dilution with 1/T of Acetic acid with (water + DMF) in different temperatures. This plot helps up to calculate Solvation activation energy for these processes.

Fig 24 to Fig 29 shows the Plot of logKa with 1/T of Acetic acid with (water + AN) at 10%, 20%, 40%, 50%, 60% & 80% proportions in different temperatures. These plots help us to calculate the change in enthalpy for these solvation processes.

Fig 30 shows Plot of logλm at infinite dilution with 1/T of Acetic acid with (water + AN) in different temperatures. This plot helps up to calculate solvation activation energy for these processes.

Fig 31 to Fig 34 shows the plot of of log Molar Conductance vs log C from 288K to 318K of Acetic acid with (water + DMF) to determine the slopes.

Fig 35to Fig 38 shows the plot of of log Molar Conductance vs log C from 288K to 318K of Acetic acid with (water + AN) to determine the slopes.

These plots help us to determine the ion-pair formation in equilibrium conditions according to Fuoss equation.

From the above studies it was observed that ion-solvent interaction occurred both the medium. And also ion-pair formation happened in equilibrium conditions. ΔG, ΔS and ΔH value support these type interactions.

Conclusions

From the above study it was observed that at higher temperature for both the systems limiting conductance value increases, as well as dissociation constant (Kc) decreases. From association constant (Ka) values we have seen that at low to high temperature Ka value increases. So, at lower temperature Kc value increases as well as ion-solvent interaction increases. Activation salvation energy for both the systems i.e, AcOH with (water+DMF) and (water+AN) were comparable values. In different proportions, Ka value increases at higher temperature. For AcOH with (water+DMF), at 60% and 80% Ka value was much higher than that of other proportions. For AcOH with (water+AN), at 80% Ka value was increases than the other proportions. Thermodynamic data supports our ion-solvent interaction study. Negative value of ΔG indicated the spontaneity of this study. At higher temperature ΔS value was to some extent increases. According to Fuoss, ion-pair formed in

equilibrium conditions for both these systems in different proportions in different temperatures. But from these thermodynamic parameters it was concluded that these ion-solvent interactions studies were not entrophically favourable.

Acknowledgements

Authors are thankful to the Principal as well as Dept of Chemistry, A.K.P.C. Mahavidyalaya for all kind of necessary supports. Also thankful to Mr. Sandip Hazra, Deputy General Manager, Tata Motors, Pune always helps me for this study.

References

1. A. Hazra, Int Journal Scientific & Technology Research, 4 (2013), 99.
2. A. Hazra, Int Journal Scientific & Technology Research, 3 (2014), 326-332.
3. A.Hazra, A.Malik and A. Pan, ACJ, Vol IX, Issue IV(2020) P 4269-4285
4. Parvatalu D and Srivatsava A K, J Chem Eng Data, 48(2003) 608.
5. Bester Roga M, Neuder R & Barthel J, J Solution Chem, 29 (2000) 51.
6. Szejgis A, Bald A, Gregorowicz J & Zurada M, J Mol Liq, 79 (1999) 123.
7. Das B & Hazra D K, J Solution Chem, 27 (1998) 1021.
8. Yokoyama H & Ohta T, Bull Chem Soc Jpn, 61(1988) 3073 and references therein.
9. Hogfeldt E, Stability Constants of metal ion complexes [Pargamon Press, Part A] 1982.
10. Pethybridge A D & Spiers D J, J Chem Commun (1974) 423.
11. Susha C B & Ishwara Bhat J, Indian j Chem, 35A (1996) 305.
12. Ishwara Bhat J & Kishore Shetty M, J Chem Eng Data.(In Press).
13. Sreelatha T N, Solvation behaviour of Bismuth compounds as a function of dielectric constant, Ph.D Thesis, Mangalore university, Mangalore, 2003.
14. Ishwara Bhat J & Shreevaraprasad N S, Oriental J Chem, 19(2) (2003) 381.
15. Bockris J O M & Reddy A K N, Modern Electrochemistry, Vol 1 (Plenum Press, New York), 1998.
16. D. M. Rao, C. Kalidas, Z. Naturforsh, 45A (1990) 1006-1009.
17. https: // en.m. Wikipedia.org
18. C. A. Karus, W.C. Bray, J. Am. Chem. Soc. 35 (1913) 1315-1434.
19. T. Shedlovsky, J. Franklin Inst. 225 (1938) 739-743.
20. R. M. Fuoss, C. A. Karus, J. Am. Chem. Soc. 55 (1933) 476-488.