The Electrical Conductivity of HCl in Binary Solvent Mixtures – A Probe for its Molecular Interaction Study

[1]S. Jagan Raj, [2]J. Subha, [3]S. Bangaru Sudarsana Alwar and [4]P.S. Raghavan

[1]Department of Chemistry, Velammal Institute of Technology, Panchetti, Chennai
[2]Department of Chemistry, R.M.D Engineering College, Kavaraipettai, Chennai
[3]Department of Chemistry, D.G. Vaishnav College, Arumbakkam, Chennai
[4]Department of Chemistry, Madras Christian College, Tambaram, Chennai
Email : sjaganraj27@gmail.com

Abstract: The dissociation constant values of hydrochloric acid in binary solvents, such as alcohol and water were studied by conductometric method. Its equivalent conductance values at infinite dilutions have been determined graphically using ORIGIN 61 program. These hydrochloric acid mixtures were studied at various concentrations in combination of ethanol-water mixtures with ethanol proportions 5%, 10%, 15%, 20%, 25%, 50% and 80% . The average K_a values were calculated and the extent of alcohol content to its K_a values was graphically plotted. The graphical values show the effect of certain important solvent properties that affect electrolyte dissociation. Moreover, variation in the K_a values obtained over the whole composition range studied was explained by means of preferential solvation of hydrochloric acid in alcohol-water mixtures. The results are in concordance with determination of K_a values of hydrochloric acid in single solvent study. Furthermore, the influence of the solvents on the dissociation constant values has been discussed. Thus, an overview of the solvent effects on the molecular liquid structure is examined. The general effect of the variation in concentration of hydrochloric acid in alcohol-water mixtures on the values of dissociation constant in these media is also described.

Keywords: Conductometry, HCl catalysed reactions, Binary solvent mixture, Degree of dissociation.

I. INTRODUCTION:

Conductometric studies provide useful and important indications of solvent structure, ion-solvent interaction and ion-ion interaction. There are several conductometric measurements that have been reported in literature; however such studies in mixed solvents are relatively rare [1]. It is shown that solvent blending or co solvency plays a major role in relating the characteristics of a solute in a solution [2]. Some of these may be its stability, solubility and dissociation constants.

Solvent composition plays a vital role in the conductivity of an electrolyte [3]. In recent years there has been an increasing interest in the study of behaviour of electrolytes in partial and non aqueous solvents [4-6]. It targets on investigating the role of a solvent in the solvation of an ion. There is indeed a special focus in learning the behaviour of ethanol water mixtures. Of mixed solvent systems, ethanol-water mixtures are highly unique. They are different from other alcohol + water mixtures. It is reported that in relatively dilute alcohol the rate gets inversely proportional to the viscosity of the mixture [7]. In this paper, we report the varied conductometric results of HCl in dilute and concentrated forms in several combinations of ethanol water mixtures ranging from 0% - 80%. Ethanol – water binary mixtures are always suitable systems for studying the ionization processes of acids. These mixed solvents provide a suitable media for chemical reactions. They are also powerful solvents for many organic and inorganic compounds. HCl is a very useful reagent in organic and inorganic synthesis [8]. Its industrial applications are related to the H^+ and Cl^- polarity / dissociation.

Solvent – solvent interactions may have predominant effects on solute – solvent interactions. The solute may get solvated preferentially by any one of the solvents present in the mixture [9]. The solute – solvent interactions in water-organic media has been systematically reported by several researchers [10-12]. Considerable work has been reported on the solute-solvent interactions in water-organic media from measurements on the dissociation constants and enthalpies for weak acids in water-rich mixtures containing alcohol [12-13].

HCl catalysed reactions generally recommend the myth that HCl is a strong acid. i.e., dissociation is fully complete as HCl is completely soluble in water. Hence the importance of HCl as a catalyst is not studied, at large. On the contrary, HCl catalysed reactions in binary solvents break the myth that HCl is always a strong acid; hence solvent polarity which affects the dissociation of HCl, and its rate in turn is an immediate question of

task. It is also assumed that solvents used under similar conditions have the same dielectric constant and same rate values. Henceforth, the nature of the solvent becomes very important in studying the kinetics of a reaction. Thus HCl, a strong acid can only be an assumption for acid catalysed hydrolysis reactions, where the ester is completely soluble in water. For other organic reactions, where HCl catalyses a reaction, the [H^+] may get solvated. When compared with general base catalysed hydrolysis for instance, when NaOH is used in water as a solvent, its rate changes are moderate. But when the solvent gets replaced by DMSO the rate becomes too high, the reason attributed to the fact that water completely solvates the base, but in the latter case DMSO solvates the base initially and also de-solvates it immediately. NaOH becomes free then and OH^- becomes hyperactive increasing the rate of such reactions.

Thus we conclude the fact that the characteristics of HCl are reduced from being a strong acid at all conditions. Thus the solvent used decides its polarity and also introduces it, a dissociation constant.

The aim of this work is to investigate the dissociation properties of HCl in mixed solvent systems. This in turn, reflects the solvent effects, dielectric properties and solute solvent interactions in particular. This work presents the study of solvent composition of the reaction kinetics of HCl in liquid phase reactions. An interesting observation is that during the reaction the composition of the bulk solvent properties mechanically changes the behaviour of HCl reactivity. In this paper our efforts have been precisely dedicated to the analysis of the influence of HCl composition in binary solvents comparing the extent of dissociation (α) to the rate constant values taken from literature and comprehend it with the dissociation parameters for dilute and concentrated HCl at varied combinations of ethanol-water mixtures.

II. EXPERIMENTAL:

2.1 Materials:

Absolute ethanol of Analar Grade (purity 99.8%) obtained from Shanghai Chemical Corporation china was used. The specific conductance of the triply distilled water used was less than 10^{-6} S cm^{-1}. Binary mixtures of ethanol-water were prepared by directly pipetting the constituent components in a graduated pipette. HCl used was standardised using a primary standard namely Na_2CO_3. Ultra pure methyl orange indicator of Fischer Scientific Ltd was used. Solutions of the HCl alcohol water mixtures were prepared in a dilute range of HCl from 0.01098 N – 0.001098 N. A complimentary set of HCl alcohol water mixtures were also prepared in a concentrated range of HCl ranging from 1M-0.3M.

2.2 Methods:

A highly precise digital conductometer, Model CDM 230 and a conductivity cell were used for conductivity measurements. The cell constant of the conductivity cell used was accurately determined using freshly prepared KCl solutions. The cell constants were determined by calibration with aqueous KCl solutions, as recommended [14-15]. The cell constant of the cell used was 0.92 cm^{-1} with an uncertainity of 0.01 %. Their electrodes were platinised to minimize polarisation effects [16].

Solutions of HCl have been prepared by exact proportions in alcohol-water mixtures ranging from 0-80%, in dilute and concentrated forms at 303 K.

Computation:

The conductance data have been analysed by means of the specific conductance formulae.

K= (Conductance) (l/a) expressed in S cm^{-1}, where l/a is the cell constant (in cm^{-1}) of the given cell containing the solution being measured.

The equivalent conductivity λ was then determined by the formula $K_s \times \dfrac{1000}{C}$ where C is the equivalent concentration. On decreasing the concentration of HCl, increase of the λ values were observed. This is attributed to the decrease of the viscosity of the mixtures. The molar conductance at infinite dilution was obtained by using Kohlrausch's law by plotting λ vs. √c. Later its degree of dissociation α was calculated using the formula $\alpha = \dfrac{\lambda}{\lambda_\alpha}$. Its K_a values were subsequently measured using the Oswald dilution law,

$$K_a = \frac{C\alpha^2}{1-\alpha}$$

The average of dissociation constants was taken. These set of measurements and calculations were performed for HCl-ethanol water mixtures ranging from HCl concentrations of 1 M to 0.8 M, 0.5M, 0.3M, 0.0109M, 0.0087M, 0.0065M, 0.0054M, 0.0032M, 0.0021M and 0.0010M . The present study investigates both concentrated and the most dilute forms of HCl to know the changes caused by such binary mixtures in its conductance and ionisation behaviour to highlight about its molecular structural changes. The percentage compositions of ethanol present in such solutions were 0%, 5%, 10%, 15%, 20%, 25%, 28%, 40%, 50%, and 80% . The choice of such ethanol proportions began in 5% increments and continued at 28%, 40%, 50% and one higher ethanol proportion, 80%. Such a high ethanol medium was selected to learn the nature of HCl acitivity at such concentrations also. The average K_a values from literature [17] were taken and plotted against the % of alcohol content for both dilute and concentrated forms of HCl. To know the kinetics of such an HCl catalysed reaction the degree of dissociation α was plotted against the % of alcohol content. Comparative tabular columns (Tables 2 and 3) were given differentiating the average K_a values of HCl with % of alcohol content in both

_____
ISSN (Print):2347-7601, ISSN (Online): 2347-761X, Volume -2, Issue -1, 2014

35

dilute and concentrated forms. The experimental results proposed are in good agreement with the values found in literature [3].

III. RESULTS AND DISCUSSION:

To learn the kinetics of such HCl catalysed reactions in ethanol water mixtures, the rate constant values of alcohol % at 0, 9, 18, 28, 40 and 50% for the acid catalysed [1M] hydrolysis of ethyl acetate were taken from literature)[17] and compared against the measured α values for both sonic and non sonic forms. It could be observed from Table 1 that the values indicate the fact that higher the alcohol content, the extent of dissociation α decreases considerably first and then increases gradually.

Table 1: α values of 1M HCl against the rate constant values at several proportions of ethanol water mixtures.

% Ethanol in water	Rate Constant k X105s-1		α
	Non Sonic	Sonic	
0	9.56	12.4	0.2730
9	6.91	8.01	0.2573
18	5.62	5.8	0.3177
28	5	6.78	0.2439
40	3.23	7.48	0.3540
50	2.37	5.76	0.4472

From the rate constant graphs drawn, it was observed that under non-sonic conditions, when the rate constant values were plotted against α, the plot showed a linear decrease. This trend in values is graphically depicted linear fit in Figure 1.
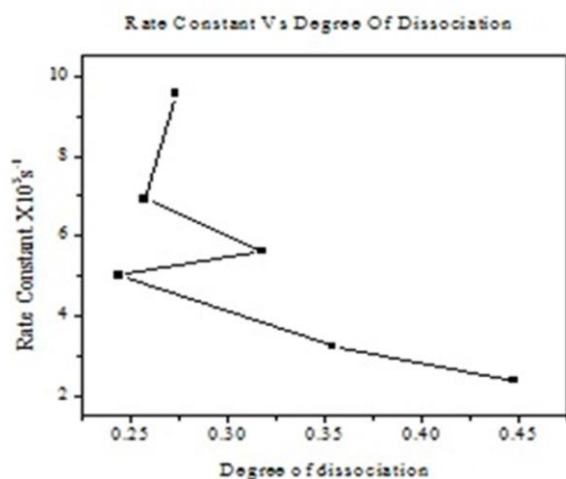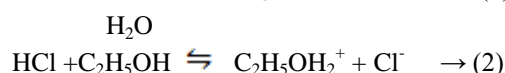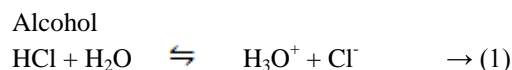

Figure 1: Non sonic Conditions (Rate Constant k x 10^5 s^{-1} Vs Degree of dissociation for 1M HCl)

The solvent mixtures play a major role in identifying the behaviour of HCl, reducing its strong acid behaviour.

Thus it is also assumed that at lower % of alcohol content, HCl in alcohol water mixtures acts like an emulsion where HCl is surrounded by majority of water molecules and only traces of alcohol. Sclar etal.,[18] reported that the comparatively low rates in absolute alcohol indicate the fact that the proportionality does not hold over the entire range of alcohol concentration. The present study also proves that the values deviate at few concentrations. But when the % of alcohol ranged from 25% onwards, HCl was solvated by alcohol predominantly and the reverse of the above occurred. Hence, it is observed that α increases on higher alcohol concentrations.

These results could be explained based on 2 conditions. When HCl catalyses a binary solvent mixture one of the following reactions occurs:

Alcohol

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^- \quad \rightarrow (1)$$

$$H_2O$$

$$HCl + C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + Cl^- \quad \rightarrow (2)$$

At lower alcohol proportions (alcohol % < 20%), equation (1) predominates and at higher alcohol proportions, equation (2) predominates. Our assumption towards the mechanism of such increasing α value can be obtained by substantiating the above results with the tabulated rate constant values. It is observed that greater the alcohol content greater the α values. As the α values become higher the rate constant values show a linear decrease, as in figure 1. Thus the effect of solvent primarily leads a major role in deciding the kinetics of a reaction giving light to the differential nature of HCl and its activity. When the percentage of alcohol content increases the α values also show a tremendous increase. This is attributed to the fact that at higher % of alcohol, the nature of the solvent ethanol changes its characteristics to a base facilitating step 2. The highly concentrated HCl solution dissociates the proton readily and the alcohol now changes its nature from a solvent to a base extracting the proton easily. This consequently increases the α values. Hence it could be concluded that the fact that the behaviour of HCl as a strong acid has been considerably reduced.

The same explanation holds good for the study of rate constant graphs under sonic conditions also.

The graphs and values support linearity excepting the spotted values which record for further argumentation that claims molecular structure study at such alcohol proportions.

We also took an effort in plotting the degree of dissociation against the % of alcohol content values for dilute and concentrated solutions of HCl at varied ethanol-water proportions. The results for the dilute solutions of HCl alcohol water mixtures are represented in figures 2, 3 and 4.

_____
ISSN (Print):2347-7601, ISSN (Online): 2347-761X, Volume -2, Issue -1, 2014
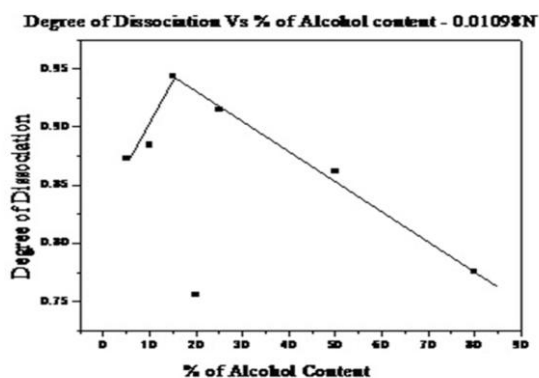
36

Figure 2: Degree of dissociation vs. Percentage (%) of alcohol content - 0.01098 N HCl
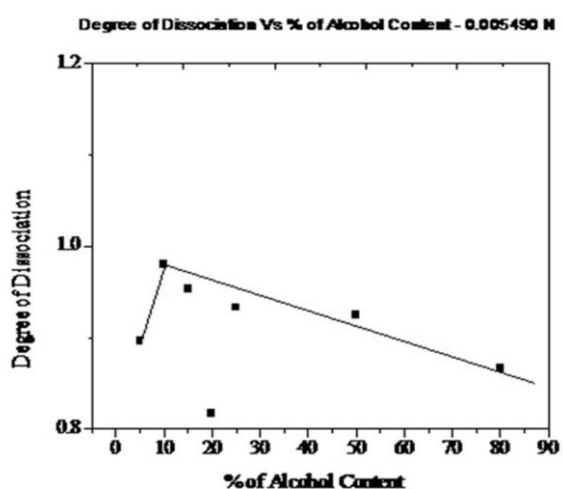

Figure 3: Degree of dissociation vs. Percentage (%) of alcohol content - 0.005490 N HCl
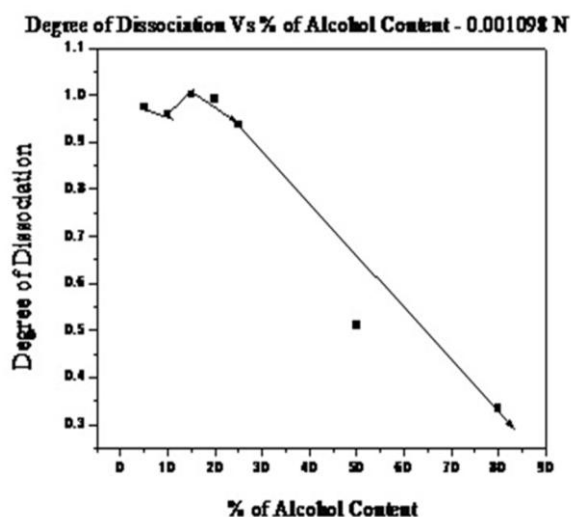

Figure 4: Degree of dissociation vs. Percentage (%) of alcohol content - 0.001098 N HCl

The figures 2, 3 and 4 obtained for the dilute solutions of HCl at varied ethanol water proportions show an increase in α value first followed by a steep decrease

downward. The ions that contribute towards conductance are H^+, Cl^- and H_3O^+ at lower alcohol proportions, and H^+, Cl^- and $C_2H_5OH_2^+$ at higher alcohol proportions. As the ion $C_2H_5OH_2^+$ is a bulky ion, its contribution towards conductance becomes minimum due to decreased ionic mobility. Literature studies prove the fact that the addition of ethanol into the HCl binary system worsens the stabilization of the charged particles formed and thereby lowers the dissociation [11]. The values observed in the present work are in perfect agreement with the literature values. It is hence graphically represented as a steep decrease in α value at higher alcohol combinations (> 50%).

A comparative tabular column is provided for both dilute and concentrated forms of HCl at several ethanol - water mixtures giving its α and K_a values. These values are provided in Table 2 and 3.

Table 2: Comparative Analysis of α, Ka, λα for Dilute HCl in Ethanol Mixtures (5% - 80%)

S.NO	%EtOH	[HCl]	α	Ka	λα
1	5%	0.0109	0.8743	0.0668	436.65
2		0.0087	0.8806	0.0570	
3		0.0065	0.8722	0.0392	
4		0.0054	0.8977	0.0432	
5		0.0043	0.9455	0.0720	
6		0.0032	0.9112	0.0308	
7		0.0021	0.9169	0.0222	
8		0.0010	0.9765	0.0445	
9	10%	0.0109	0.8929	0.0818	403.64
10		0.0087	0.9699	0.2747	
11		0.0065	0.9742	0.2431	
12		0.0054	0.9896	0.5184	
13		0.0043	0.9666	0.1229	
14		0.0032	0.9574	0.0708	
15		0.0021	0.9654	0.0592	
16		0.0010	0.9689	0.0331	
17	15%	0.0109	0.9553	0.2244	381.17
18		0.0087	0.9661	0.2421	
19		0.0065	0.9626	0.1635	
20		0.0054	0.9651	0.1465	
21		0.0043	0.9754	0.1703	
22		0.0032	0.8749	0.0201	
23	20%	0.0109	0.7459	0.0240	418.43
24		0.0087	0.7912	0.0263	
25		0.0065	0.7881	0.0193	
26		0.0054	0.8059	0.0183	
27		0.0043	0.8219	0.0166	
28		0.0032	0.8088	0.0112	
29		0.0021	0.8491	0.0105	
30		0.0010	0.9790	0.0502	
31	25%	0.0109	0.9304	0.1367	323.47
32		0.0087	0.9445	0.1412	
33		0.0065	0.9347	0.0882	
34		0.0054	0.9488	0.0966	
35		0.0043	0.9785	0.1964	
36		0.0032	0.9946	0.6059	
37		0.0021	0.9778	0.0948	

38		0.0010	0.9534	0.0214	
39	50%	0.0109	0.8774	0.0689	137.1
40		0.0087	0.8736	0.0530	
41		0.0065	0.8650	0.0365	
42		0.0054	0.9418	0.0837	
43		0.0043	0.9418	0.0669	
44		0.0032	0.9305	0.0410	
45		0.0021	0.9316	0.0278	
46		0.0010	0.5149	0.0006	
47	80%	0.0109	0.7900	0.0326	54.09
48		0.0087	0.7817	0.0245	
49		0.0065	0.8987	0.0525	
50		0.0054	0.8827	0.0364	
51		0.0043	0.7835	0.0124	
52		0.0032	0.9153	0.0326	
53		0.0021	0.9145	0.0214	
54		0.0010	0.3400	0.0001	

Table 3: Comparative Analysis of α, Ka, $\lambda\alpha$ for Concentrated HCl in Ethanol Mixtures (5% - 80%)

S. No.	%EtOH	[HCl]	α	Ka	λα
1		1	0.2730	0.1025	
2	0%	0.8	0.3267	0.1268	447.32
3		0.5	0.4668	0.2043	
4		0.3	0.6043	0.2769	
5		1	0.2632	0.0940	
6	5%	0.8	0.3199	0.1204	442.28
7		0.5	0.4626	0.1991	
8		0.3	0.5984	0.2675	
9		1	0.2573	0.0892	
10	9%	0.8	0.3162	0.1170	436.02
11		0.5	0.4481	0.1820	
12		0.3	0.6001	0.2702	
13		1	0.3177	0.1479	
14	18%	0.8	0.3908	0.2006	355.65
15		0.5	0.5491	0.3344	
16		0.3	0.6131	0.2915	
17		1	0.2439	0.0787	
18	28%	0.8	0.2879	0.0931	412.85
19		0.5	0.4026	0.1356	
20		0.3	0.6039	0.2763	
21		1	0.3540	0.1939	
22	40%	0.8	0.4382	0.2734	233.36
23		0.5	0.5374	0.3121	
24		0.3	0.6528	0.3682	
25		1	0.4472	0.3618	
26	50%	0.8	0.5166	0.4417	182.68
27		0.5	0.6339	0.5488	
28		0.3	0.6897	0.4600	
29		1	0.4414	0.3487	
30	80%	0.8	0.5501	0.5380	80.17
31		0.5	0.6444	0.5838	
32		0.3	0.6920	0.4663	

It is seen that the limiting molar conductance varies with increasing ethanol proportions [12]. The results are also in accordance with the study of conductance behaviour of citric acid in water ethanol mixtures reported [19].

Similar set of graphs were obtained for concentrated solutions of HCl. The results are represented in figures 5-8.
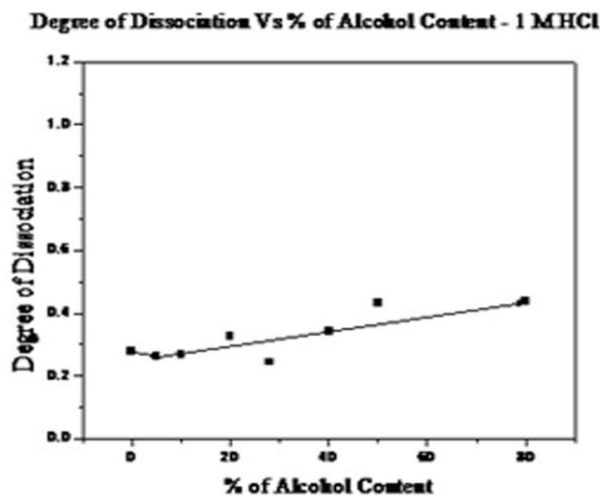

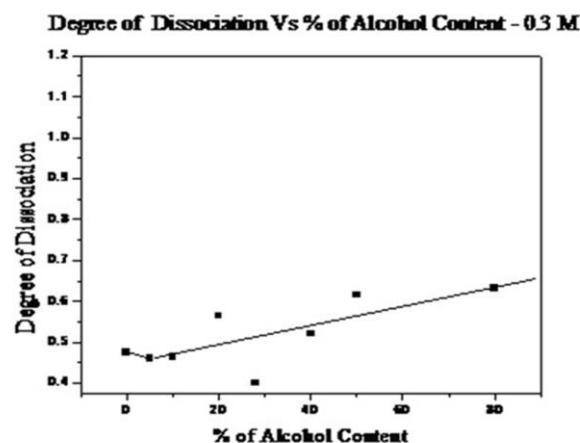Figure 5: Degree of dissociation vs. Percentage (%) of alcohol content – 1M HCl

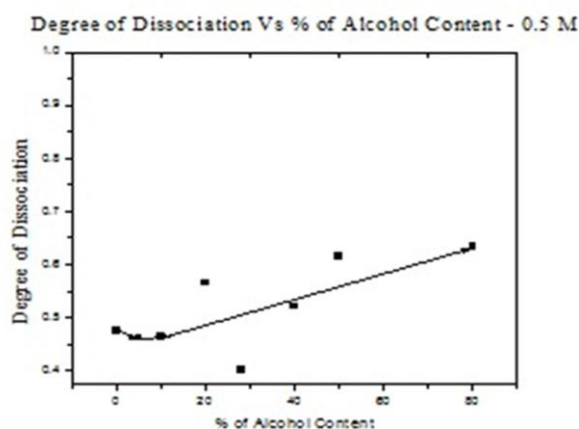Figure 6: Degree of dissociation vs. Percentage (%) of alcohol content – 0.3M HCl

Figure 7: Degree of dissociation vs. Percentage (%) of alcohol content – 0.5M HCl

_____
ISSN (Print):2347-7601, ISSN (Online): 2347-761X, Volume -2, Issue -1, 2014
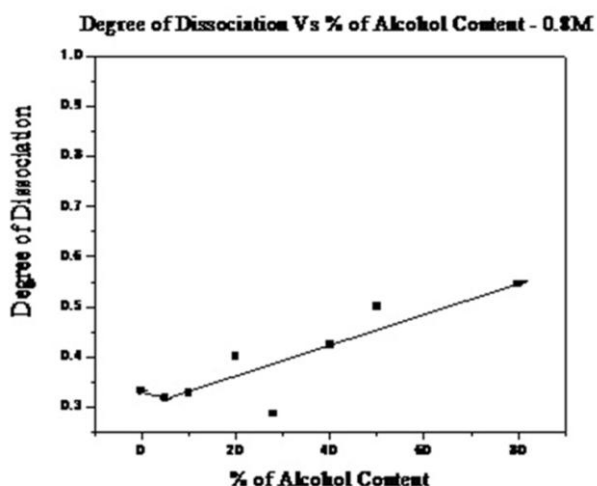
38

Figure 8: Degree of dissociation vs. Percentage (%) of alcohol content – 0.8M HCl

The results prove the fact that at lower alcohol proportions HCl behaves as a strong acid with perfect ionisation but at higher alcohol proportions the second equation predominates which includes conductance of H^+, Cl^- and $C_2H_5OH_2^+$ ($C_2H_5OH_2^+$ contribution is negligible). Hence dissociation increases steeply. As explained earlier, the solvent ethanol at higher proportions assumes basic behaviour extracting the proton readily from [1 M] HCl.

The same reason for increase in α value with decrease in rate constant values holds good here also. The deviation due to skipped points supports further argumentation. Hence it is accounted that when the alcohol content is varied ranging from 0-80%, for HCl at dilute concentration, the ionisation values (α) increased first and then decreased. The pronounced deviation at 20% in every concentration supports further study that relates to its molecular structure [17].

IV. CONCLUSION:

It is observed that the concentration dependence of ionic mobility in alcohol – water mixtures is in accordance with theories based largely on ionic electrostatic forces of the solvent mixtures.

Hence we conclude stating 3 important observations. The kinetics of an HCl catalysed reaction is predominantly decided by its solvent composition and dielectric constant. The experimental results for the ionization values of dilute HCl in varied ethanol water mixtures have been presented as a function of rate constant values and different percentage composition of (ethanol + water) mixed solvent media. The ionization values increased first and then decreased.

It is also observed that the addition of co solvent to water results in a competition for hydrogen bonding with water by the cation and co solvent by the anion. This tends to remove some of the water molecules from the solvation shell of cation or anion. It is evident that the limiting conductance for dilute HCl and concentrated

HCl in ethanol water mixtures decreases with increasing ethanol proportions, because of the increase in effective ionic size of the solvation shell.

The ionization values for concentrated solutions of HCl at various alcohol proportions, increases linearly first, followed by a gradual increase. It throws light on the idea that HCl should be moderately associated in general terms, whereas in a medium of ethanol - water mixtures, the reactivity of HCl accounts for changes from reducing the strong acid characteristics of the solute.

REFERENCES:

[1] Janz, G.T.,Tomkins., R.P.T.: Non. Aq. Electro.Handbook, Academic Press,. London, Vol.1, (1972).

[2] Abolghasem Jouyban, Hak-kim Chan, Brian J. Clark, William E. Acree, Jr.: Mathematical representation of apparent dissoication constants in aqueous-organic solvent mixtures. International Journal of Pharm. 246, 135-142 (2002).

[3] George Moumouzias and George Ritzoulic. Electrolytic conductances of Tetrabutylammonium Tetraphenylborate in propylene carbonate + Acetonitrile mixtures at (25,30 and 35)° C. J. Chem. Eng. Data , 41, 326-330 (1996).

[4] Radhika V., Manikyamba. P.: Conductance and solvation behaviour of benzimidazolium dichloromate in Dimethyl sulphoxide – Water mixture. Indian J. Chem. 2008; 47[A]: 1814-1817, (2008).

[5] Ishwara Bhat J, Sree latha TN,:Effect of Ethanol on the solvation behaviour of BI_3 in acetonitrile, methanol and DMF as a function of temperature. J. Mol. Liq: 116[3]:175-180. (2005).

[6] Dip Singh Gill, Anand H, Kumari A, Puri JK.: Study on the Comparitive solvation behaviour of Na^+ and Cu^+ cations in acetonitrile + N,N dimethyl formamide mixtures at 298;15K.Z., Natur forsch ; 59[9]; 615-620. (2004).

[7] Morel.J.P., Fauve.J., Avedikian.L., Juillard.J,: Solutes-Solvent interactios in water-tert-butyl alcohol mixtures III.ΔG°,ΔH° and ΔS° for dissociation of aliphatic carboxylic acids in water-rich media. J. Solution Chem. 3 , 403. (1974)

[8] Islam, M.R., Ansari, A.S.: The Electrical Conductivity of Tetra alkyl ammonium Electrolytes in Isopropanol –Water Mixtures at 25°C .Indian J.Chem. 28A, 486 (1989).

[9] Christensen.J.J.,Izatt R.M., HansenL.M., "A Thermometric Titration Procedure for Determination of Consecutive Heats of Complex Ion Formation," Proceedings of the Seventh

International Conference of Coordination Chemistry, Stockholm, Paper 7 Fl, 344-346 (1962).

[10] Banan A. Akrawi., Amel G. Abed., Shatha M. Quba.: Electrical Conductivity of [Co(en)$_2$Cl$_2$]Cl in Mixed Solvents (Alcohol+water) at 298 K......Raf Jour. Sci., 17, 104-120(2006).

[11] Qun-Fang Lei, Wen-JunFang.:Enthalpic and entropic contributions to dissociation of halogen acetic acids and linear free energy relationship in EtOH-H$_2$O mixtures at 298.15 K. Thermochimica Acta 421 185-192. (2004).

[12] Ishwara Bhat,J., and Manjunatha.M.N..:Conductometric studies on solvation behaviour of sodium citrate in water +methanol and water+ ethanol at different temperatures Indian Journal of Chemical Technology Vol.17, November. pp.462-467(2010).

[13] Rodante.F.,Rallo.F.,, Fiordiponti.P.: Ionisation enthalpy of Benzoic acid in water-dimethyl sulfoxide mixture, Thermochim Acta 9 ,269. (1974).

[14] Wu, Y. C; Koch, W.F. Absolute determination of electrolytic condutivity for primary standard KCl soltuions from 0 to 50°C. J. solution Chem. 391, 20 (1991).

[15] Wu, Y.C; W. F.; Hamer, W.J; Kay, R.L.Review of electrolytic conductance standards. J. Solution Chem. 16, 985, (1987).

[16] Johnes G., Christian,S.M.: The measurement of the conductance of Electrolytes.VI.Galvanic Polarization by alternating current.J Am.Chem.Soc.,57:272(1935).

[17] Tuul mets.A., Salmar.S.: Effect of ultrasound on ester hydrolysis in aqueous ethanol. Ultrasonics Sonochemistry 8, 209-212 (2001).

[18] Schlar., Kilpatrick.: Dissolution and Diffusion. Rates in Alcohol-water Mixtures http://pubs.acs.org/59,584(1937).

[19] Ishwara Bhat.J., ManjunathaM.N.: Effect of Dielectric constant on the solvation of sodium citrate. Int. J. Chem Res, 3, 6-14 (2012).

❖❖❖