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Acceptor Number Induced NMR Chemical Shift in Chloroform

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Solvents have shown to have direct effect on NMR chemical shifts. Acceptor number, a measure of electrophilicity of a solvent, could cause a dramatic upfield or down field shift for a C-H bond. This study shows that there is a direct relation between acceptor number and chemical shifts. Binary solvents effect, though expected to be, is not constructive and doesn't show any competition for the shift but for each solvent.

Key Words: Acceptor number, NMR, Chemical shift, Chloroform.

INTRODUCTION

Gutman introduced the concept of acceptor number (AN) and donor number (DN)[1,2] as a measure of acidity or basicity respectivety. This concept was challenged later not to be comprehensive enough, however, it provided enough information regarding the behaviour of a solvent toward a solute. Much work has been done to show the solvent effect[3-8]. Studies conducted is generally based on magnetic spins or shifts due to hydrogen bonding and diamagnetic effect. The present study is based on the acceptor number effect on the NMR chemical shift.

EXPERIMENTAL

All chemicals used were of analytical grade reagents and the NMR was Bruker 80 MHz. For single solvent effect, series of solutions containing chloroform and increasing amount of different solvents were prepared. All solutions should have constant volume of 2 mL. In binary solutions, 100 µL of chloroform was added to a flask and different volume of each solvent was added to reach the final volume of 2.1 mL. For example, in 2-propanol acetonitrile mixture, solution number 10 contains 0.9 mL 2-propanol, 1.1 mL acetonitrile and 0.1 mL chloroform. Solution no. 1

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contains 0 mL 2-propanol and solution no. 21 contains 0 mL acetonitrile. Care was taken to choose the solvents that have great difference in their acceptor number so that a clear shift could be observed.

RESULTS AND DISCUSSION

Acceptor number is a measure of electrophilicity of a solvent. This number shows the behaviour of a solvent toward other species. The present studies showed that the greater this number is the greater shift it causes in a magnetic field. Table-1 shows this increase in NMR shift for chloroform. With a possible exception of water which actually reduces the wave absorption in provided magnetic field. This may be due to inorganic nature of water that prohibits inter spherical interaction with chloroform, so there is no down field shift and perhaps due to unshared pairs of electrons in water molecule. The slight shielding occurs could account for the up field movement.

TABLE-1
EFFECT OF SOLVENT ON THE NMR CHEMICAL SHIFT BASED ON THEIR ACCEPTOR NUMBER

	Solvent	AN	NMR Induced shift
1	Chloroform	23.1	7.25773
2	Diethyl ether	3.9	7.32917
3	Benzene	8.2	7.33503
4	Carbon tetrachloride	8.6	7.35032
5	Acetone	12.5	7.40479
6	Acetonitrile	18.9	7.45186
7	DMSO	19.3	–
8	Methylene chloride	20.4	7.28535
9	2-Butanone	29.1	7.22103
10	Propanone	33.5	7.42085
11	Ethanol	37.1	7.51438
12	Methanol	41.3	7.58235
13	Water	54.8	7.23987

Apart from this deviation, there is an increase in down field shift of C-H absorption with some acceptable variation which could be due to instrumental and environmental effects. Further study of one solvent effect is shown on Table-2. in which three different solvents are presented. It appears that neat solution of chloroform has a C-H absorption around δ = 7.24-7.25 ppm. Data shows that the chemical shift caused by ethanol with AN = 37.1 is higher than that of carbon tetrachloride and benzene with AN of 8.6 and 8.2, respectively.

TABLE-2
INDUCED CHEMICAL SHIFT DUE TO DIFFERENT CONCENTRATION OF THE SOLVENTS

	C_2H_5OH AN = 37.1	CCl_4 AN = 8.6	C_6H_6 AN = 8.2
1	7.49617	7.33503	7.24839
2	7.43987	7.26717	7.24994
3	7.44827	7.24588	7.24915
4	7.46965	7.25014	7.24858
5	7.46182	7.24732	7.25050
6	7.43871	7.23120	7.25125
7	7.43360	7.23228	7.25517
8	7.41844	7.25070	7.25291
9	7.40911	7.26050	7.25516
10	7.37787	7.24270	7.25287
11	7.38360	7.30440	7.25291
12	7.35968	7.30930	7.25542
13	7.3630	7.29993	7.25500
14	7.31831	7.32845	7.25612
15	7.32735	7.33023	7.25711
16	7.30892	7.32880	7.25252
17	7.29965	7.33370	7.24917
18	7.28202	7.34100	7.24632
19	7.27197	7.34590	7.24932
20	7.25544	7.25340	7.25879

Total volume is 2 mL, Chloroform concentration increased From 5 to 100 % solution No. 10 contained 1 mL chloroform and 1 mL solvent.

A closer look at each solution shows that as the concentration increases the chemical shift and *vice versa*. However, the difference in chemical shift for chloroform in each solvent clearly shows that the interaction between each solvent and chloroform is due to the acceptor number effect and it is contrary to their dielectric constant shown in Table-4. The induced chemical shift in carbon tetrachloride and benzene solutions are due to their acceptor number effect, since there is little external influences exerted upon the solution system and their geometric hindrance prevents strong hydrogen bonding between chloride and hydrogen.

Binary solvent effect: The next step in present study was to ascertain the effect of binary solvents mixture on the chemical shift. Table-3 shows three systems (CCl_4:CH_2Cl_2), ((CH_3)CO:C_2H_5OH) and ((CH_3)$_2$CHOH:CH_3CN) and their effect on C-H shift of chloroform. It is natural to assume that there should be a constructive effect on the C-H shift, however, the results show otherwise. In the case of (CCl_4:CH_2Cl_2) system as the concentration of CH_2Cl_2 is 100 % and CCl_4 0 % the effect is as accepted single solvent δ = 7.28838 ppm, however, as the CCl_4 concentration increases.

Not only is the effect not constructive, but due to CH_2Cl_2 concentration reduction, there is a descending trend observed. This phenomenon could be due to the competition between the two solvents for the interaction with chloroform. An added interaction between the solvents themselves (acetone:ethanol), (2-propanol:acetonitrile) could have destructive, fewer numbers of free molecules available, effect on the chloroform chemical shift. At 50 % concentration for both solvents, the shift is halved which shows the competiveness nature of the interaction and as the CCl_4 concentration increases the effect is similar to a single solvent effect where at 100 % CCl_4, δ = 7.25112 ppm equivalent to data presented in Table-3. The same trend is observed on the other two binary systems.

TABLE-3
TWO SOLVENTS EFFECT ON THE CHLOROFORM
NMR CHEMICAL SHIFT

	CCl_4/CH_2Cl_2 AN= 8.6/20.4	$(CH_3)_2CO/C_2H_5OH$ AN = 12.5/37.1	$(CH_3)_2CHOH/CH_3CN$ AN=33.5/18.9
1	7.28838	7.41023	7.43680
2	7.28254	7.54435	7.44402
3	7.28007	7.42257	7.50095
4	7.27481	7.51386	7.49997
5	7.26991	7.51177	7.46083
6	7.26974	7.56476	7.49730
7	7.26388	7.52994	7.45823
8	7.26252	7.51839	7.46310
9	7.26175	7.57897	7.41353
10	7.26034	7.52989	7.45820
11	7.26498	7.51190	7.43112
12	7.26034	7.56289	7.52410
13	7.25736	7.65110	7.61940
14	7.25990	7.53390	7.49997
15	7.25466	7.46800	7.47691
16	7.25878	7.51814	7.57050
17	7.27088	7.40895	7.55539
18	7.27061	7.42624	7.40210
19	7.27501	7.41363	7.40160
20	7.25739	7.49205	7.39480
21	7.25112	7.49121	7.38250

Concentration of the numerator increased from 0 to 100 % and *visa versa* for the denominator.

In conclusion, Table-4 shows a comparison between acceptor number and the dielectric constant effect on the C-H chemical shift. As it is seen from the table, there is a constant increase in the chemical shift with AN

increase, however, there is a fluctuation and some degree of constancy for the dielectric constants. In general, the dielectric constant, magnetic, hydrogen bond effect studies cannot provide a clear answer to the chemical shift and the acceptor number for each compound.

TABLE-4
COMPARISON OF ACCEPTOR NUMBER WITH THE DIELECTRIC CONSTANT ON CHEMICAL SHIFT

	Solvent	NMR Shift	AN	ε
1	$CHCl_3$	7.25773	23.1	4.8
2	$(C_2H_5)_2CO$	7.39917	3.9	–
3	C_6H_6	7.31256	8.2	2.3
4	CCl_4	7.24879	8.6	2.2
5	$(CH_3)_2CO$	7.64979	12.5	20.7
6	CH_3CN	7.45186	18.9	37.5
7	CH_2Cl_2	7.28535	20.4	4.8
8	$C_2H_5COCH_5$	7.22103	29.1	18.5
9	$(CH_3)_2CHOH$	7.42085	33.5	18.3
10	C_2H_5OH	7.51438	37.1	24.3
11	CH_3OH	7.58235	41.3	32.6
12	H_2O	7.23987	54.8	80.4

Dielectric constants were taken at 20ºC.

REFERENCES

1. V. Gutman and E. Wychera, *Inorg. Nucl. Chem. Lett.*, **3**, 257 (1966).
2. V. Gutman, Coordination Chemistry in Non-Aqueous solutions, Springer, New York (1968).
3. G.E. Maciel and G.C. Ruben, *J. Am. Chem. Soc.*, **85**, 3903 (1963).
4. M. Bacon, G.E. Maciel, W.K. Musker and R. Sholl, *J. Am. Chem. Soc.*, **93**, 2537 (1971).
5. H. Fukui, *Magn. Reson. Rev.*, **11**, 205 (1987).
6. H. Dahn, *J. Chem. Educ.*, **77**, 905 (2000).
7. S.K. Khurana, V. Krishnamoorthy, S.K. Sanduja and V.S. Parmar, *Spectrochim. Acta*, **38A**, 1325 (1982).
8. R. Herzfeld and P. Nagy, *Curr. Org. Chem.*, **5**, 373 (2001).

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