CHAPTER 3.

EXPERIMENTS

In order to get into the insight of the behaviour of acetic acid in water, three complementary pieces of work were carried out, they are :

(a) Determination of the equilibrium constants

(b) A study of the heat of solvent transfer

(c) The IR study of aqueous solution of acetic acid

Each of them will be reported separately but in a semilar pattern. The results presented at the end of each section are the average values of triplicate results at 32°C. The uncertainties of those results were estimated to be less than ± 0.02 % for the NMR work and ± 0.05 % for the conductivity measurement.

3.1 Determination of the equilibrium constants

3.1.1 Chemicals

All chemicals listed below were used without further purifications.

Name	Grade of purity	Manufacturer
Acetic acid (glacial)	A.R	BDH Chemical Ltd, Poole, England.

(continued)

Name	Grade of purity	Manufacturer
DSS (2,2-Dimethyl-2-2-Silapantane-5-Sulfonate)	A.R	BDH Chemical Ltd., Poole, England.
Hydrochloric acid	Standard solution (1M)	Carlo Erba, Mirano, Italy.
Potassium chloride	A.R	BDH Chemical Ltd., Poole, England.
Potassium hydrogen phthalate	A.R	Riedel-De Haen AG Seelze-Hannover, Germany.
Sodium acetate	A.R	BDH Chemical Ltd., Poole, England.
Sodium chloride	A.R	Riedel-De Haen AG Seelze-Hannover, Germany.
Sodium hydroxide	A.R	BDH Chemical Ltd., Poole, England.

Water used in this work was first doubly distilled and then deionized using the Elgastat Unit model B114.   Typical conductance was between 1.0803×10^{-6} and 1.2534×10^{-6} $ohm^{-1}cm^{-1}$.

3.1.2 Instruments

Major instruments are given below together with their specifications.

(1) Atomic Absorption Flame Emission Spectrometer Model AA-650, manufactured by Shimadzu Corporation, Tokyo, Japan.

Specification

Slit width : range between 0-20 A° (operated at 10 A°)

Modes : flame emission and absorption

Display modes : digital read out with the printer and recorder

(2) Nuclear Magnetic Resonance Spectrometer Model FX90Q Operation (90 MHz Integrated Broadband DQD-FT NMR) manufactured by Jeol Ltd., Tokyo, Japan.

Specification

Standard magnetic field : 21100 guass.

Stability : 0.1 Hz/hr (^{13}C observation with the Hz of ^{2}D internal lock)

Long term stability : 0.8 Hz/12hrs.

Irradiation frequency : (^{1}H) 89.55~89.65 MHz adjustable in 0.1 Hz steps : (^{13}C) 22.50~22.60 MHz

Resolution : (^{1}H), (5mm tube) $\leq$ 0.2 Hz

: (^{13}C) $\leq$ 0.3 Hz

Spining side band : (^{1}H) $\leq$ 1 %

: (^{13}C) $\leq$ 2 %

Sensitivity : (^{1}H) = 70:1

(3) Conductivity Bridge

Model RC-18A, manufactured by Beckmann Instruments Inc., Cedar Grove, N.J., U.S.A.

Specification

A.C.type : generating 1 KHz and 3 KHz

Accuracy : ± 0.05 %

3.1.3 Procedure

3.1.3.1 Preparations of the solutions

The easily volatile nature of acetic acid necessitated the preparation of its solutions in water and other solvents to be done by direct weighing and to express its concentration in term of weight percent. The concentrations of other aqueous solutions namely hydrochloric acid, sodium chloride, sodium acetate, sodium hydroxide, potassium hydrogen phthalate and potassium chloride were based on molarity scale and their preparations were according to Vogel[44]. Aqueous solutions of hydrochloric acid, sodium acetate and sodium hydroxide were first prepared for the approximate concentrations. Their exact concentrations were later determined by the standard procedure given in (44) i.e. standardization of sodium hydroxide with the standard potassium hydrogen phthalate. The standardized solution of sodium hydroxide was in turn acted as the standard solution for hydrochloric acid. For aqueous solution of sodium acetate, Atomic Absorption Spectroscopy was found to be the most efficient quantitative method.

3.1.3.2 NMR measurement

The chemical shift of the aqueous solutions of acetic acid and hydrochloric acid were measured using DSS in D_2O as the external reference of the shift. The external reference was contained in a smaller NMR tube (OD = 5 mm).   The tube was then inserted into the larger NMR tube (OD = 10 mm) containing the solution undertest. Fig 3.1 shows the arrange - ment described above.
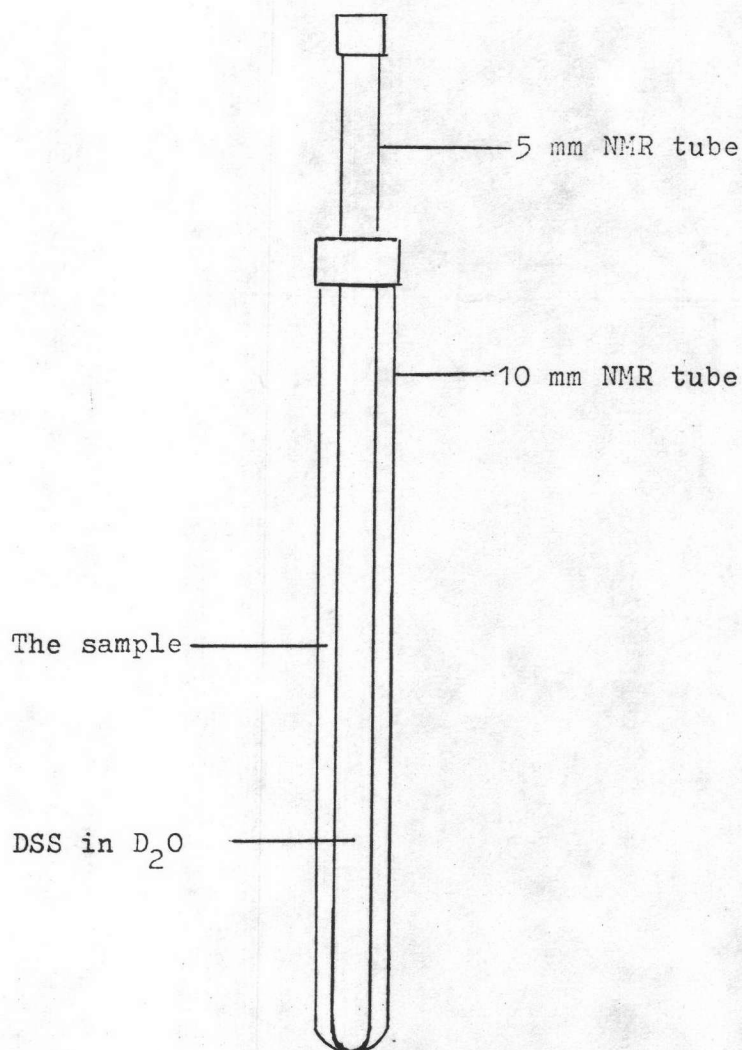

Figure 3.1 The NMR cell with the external reference.

Results of the NMR measurement at 32°C are shown in Tables 3.1 3.2 and 3.3.

Table 3.1 The proton shift of acid proton and methyl proton of acetic acid in the aqueous solution at various concentrations.

Concentration of acetic acid (%W/W)	Acid proton shift $\delta(OH)$ (ppm)	Methyl proton shift $\delta(CH_3)$ (ppm)
100.0	11.06	1.59
98.0	10.11	1.60
96.1	9.44	1.63
94.0	8.95	1.64
92.0	8.47	1.66
90.0	8.02	1.67
86.6	7.57	1.68
85.0	7.40	1.69
83.4	7.18	1.70
81.4	6.97	1.72
80.1	6.87	1.73
77.2	6.62	1.73
75.2	6.48	1.74
73.1	6.34	1.75
71.1	6.23	1.77
70.0	6.20	1.77
67.0	5.96	1.77
65.0	5.90	1.80
63.0	5.80	1.80

Table 3.1 (continued)

Concentration of acetic acid (%W/W)	Acid proton shift $\delta(OH)$ (ppm)	Methyl proton shift $\delta(CH_3)$ (ppm)
61.0	5.72	1.81
60.1	5.68	1.83
50.0	5.42	1.88
40.0	5.20	1.92
30.0	5.02	1.96
20.0	4.89	2.01
10.0	4.80	2.04
7.7	4.77	2.04
5.6	4.75	2.05
3.9	4.72	2.05
1.9	4.70	2.06
0	4.70*	-

* the shift of water proton.

Table 3.2 The carbon shift of carbonyl carbon and methyl carbon of acetic acid in the aqueous solution at various concentration.

Concentration of acetic acid (%W/W)	Methyl carbon shift, $\delta(CH_3)$ (ppm)	Carbonyl carbon shift, $\delta(CO)$ (ppm)
100.0	21.40	179.17
98.0	21.40	178.90
96.1	21.51	178.74
94.0	21.56	178.63
92.0	21.67	178.58
90.0	21.73	178.47
96.6	21.73	178.30
85.4	21.78	178.25
83.4	21.83	178.25
81.4	21.89	178.20
80.0	21.94	178.25
77.2	22.00	178.20
75.2	22.05	178.20
73.1	22.05	178.20
71.1	22.11	178.20
70.1	22.16	178.20
67.0	22.16	178.20
65.0	22.16	178.20
63.0	22.21	178.20
61.0	22.27	178.20

Table 3.2 (continued)

Concentration of acetic acid (%W/W)	Methyl carbon shift, $\delta(CH_3)$ (ppm)	Carbonyl carbon shift, $\delta(CO)$ (ppm)
60.1	22.27	178.20
56.8	22.27	178.25
54.9	22.38	178.30
52.9	22.38	178.30
50.8	22.38	178.30
50.2	22.43	178.42
46.9	22.49	178.42
44.9	22.49	178.47
42.9	22.54	178.47
40.9	22.49	178.47
40.3	22.54	178.52
30.1	22.59	178.58
27.1	22.65	178.69
25.1	22.65	178.74
23.2	22.70	178.74
21.2	22.70	178.80
20.2	22.70	178.80
10.1	22.81	178.95

Table 3.3 The proton shift of aqueous hydrochloric acid at various concentrations.

Concentration of hydrochloric acid (M)	Density (gm cm^{-3})	Proton shift δ(HCl) (ppm)
0.1358	0.9978	4.75
0.6792	1.0066	4.92
1.3264	1.0183	5.15
2.7400	1.0420	5.63
5.1010	1.0796	6.43

3.1.3.3 Conductivity measurement

On account of a higher accuracy and reproducibility of the readings attainable, the resistance mode was chosen in preference to the conductivity mode of the A.C. Conductivity Bridge.

Resistance of the aqueous solutions of hydrochloric acid, sodium chloride, sodium acetate and acetic acid were measured at both 1 KHz and 3 KHz(frequency).The conversion of the solution resistance to conductance and the correction for background solvent are treated in Appendix 7 (equations A7.1 and A7.2).

For the determination of cell constants, the method given by Jone and Bradshow[45] was followed.In this work three conductivity cells with different cell constants were used.

They are :

      (1) Cell I ,model CEL-3A,cell constant = 0.19641 cm^{-1}

      (2) Cell II ,model CEL-3D,cell constant = 4.5362 cm^{-1}

      (3) Cell III,model CEL-3D,cell constant = 3.9572 cm^{-1}

      Tables 3.4, 3.5, 3.6, 3.7 and 3.8 are prepared for the results of those measurements.

      *, ** and *** designate the resistance measured by cell I, II and III respectively.

Table 3.4 The resistance of the aqueous solution of hydrochloric acid.

Concentration of hydrochloric acid C_{HCl} (M)	The resistance, R* (ohm)		
	R(1KHz)	R(3KHz)	R(∞ Hz)
0.0002428	2905.0	2495.0	2290.0
0.0001214	4850.0	4340.0	4085.0
0.0000304	13790.0	13790.0	13790.0

Table 3.5 The resistance of the aqueous solution of sodium chloride.

Concentration of sodium chloride c_{NaCl} (M)	The resistance, R* (ohm)		
	R(1KHz)	R(3KHz)	R(∞Hz)
0.0010000	2910.0	2176.0	1809.0
0.0005000	4755.0	3720.0	3202.5
0.0002500	7770.0	6650.0	6090.0
0.0001250	12250.0	11450.0	11050.0
0.0000625	20650.0	20200.0	19975.0
0.0000312	36400.0	35700.0	35350.0

Table 3.6 The resistance of the aqueous solution of sodium acetate.

Concentration of sodium acetate c_{NaOAc} (M)	The resistance, R* (ohm)		
	R(1KHz)	R(3KHz)	R(∞Hz)
0.0049593	403.5	399.2	397.0
0.0024796	788.7	783.0	780.2
0.0012398	1550.0	1543.0	1539.5
0.0010004	1907.6	1903.0	1900.7
0.0005002	3762.0	3754.7	3751.0
0.0002501	7339.0	7329.0	7324.0

Table 3.7 The resistance of the aqueous solution of acetic acid at various concentrations.

Concentration of acetic acid	Density	Resistance, R** (ohm)		
(%W/W)	gm cm^{-3}	R(1KHz)	R(3KHz)	R(∞ Hz)
80.1	1.0573	38700.0	41000.0	42150.0
75.2	1.0576	22600.0	22400.0	22300.0
73.1	1.0566	18360.0	18360.0	18360.0
70.0	1.0562	14160.0	14130.0	14115.0
67.0	1.0548	11257.0	11236.0	11225.5
65.0	1.0543	9830.0	9810.0	9800.0
63.0	1.0537	8635.0	8621.0	8614.0
61.0	1.0528	7653.0	7650.0	7648.5
60.1	1.0524	7310.0	7271.0	7251.5
50.0	1.0464	4488.0	4480.0	4476.0
Water	0.9951	4761904.8	4000000.0	3619047.6

Table 3.8 The resistance of the aqueous solution of acetic acid at various concentrations.

Concentration of acetic acid	Density	Resistance,R*** (ohm)		
(%W/W)	gm cm^{-3}	R(1KHz)	R(3KHz)	R(∞ Hz)
100.0	1.0132	_a	_a	_a
95.0	1.0198	1724137.9	1923076.9	2022546.0
90.0	1.0250	285714.3	303951.4	313070.0
85.0	1.0292	84500.0	84500.0	84500.0
40.0	1.0398	3177.5	3175.8	3175.0
30.0	1.0305	2506.0	2505.5	2505.2
20.0	1.0194	2221.0	2220.2	2219.8
10.0	1.0074	2384.5	2384.4	2384.2
5.0	1.0014	2987.0	2985.2	2984.3
2.0	0.9974	4416.5	4415.5	4415.0
1.0	0.9959	6261.0	6260.0	6259.5
1/5	0.9951	13780.0	13765.0	13757.5
1/25	0.9951	31350.0	31300.0	31275.0
1/125	0.9951	74000.0	73000.0	72500.0
1/625	0.9951	8635.0*	8085.0*	7810.0*
1/3125	0.9951	20005.0	19710.0	19562.5

a cannot measured

3.2 Determination of the heat of solvent transfer

3.2.1 Chemicals

Analytical grade benzene and carbon tetrachloride obtained from Riedel-De Haen AG Seelze-Hannover and BDH Chemical Ltd respectively were used as two immiscible solvents.

3.2.2 Instrument : Thermostat Bath

The temperature of the bath was regulated by the temperature controller, transistorized relay and mercury probe model T-681D for the accurate temperature. For low temperature work, the temperature of the thermostat bath can be controlled to within ± 0.01 °C by means of the Beckman contact thermometer, for high temperature work, however ± 0.1 °C was the limit.

3.2.3 Procedure

100 cm^3 of 1 M stock aqueous acetic acid were pipetted into a reagent bottle (250 cm^3) and 200 cm^3 of benzene were added. The bottle was shaken for 30 minutes afterwhich it was placed in the thermostat bath which was controlled at 32 °C for 3 hrs to get to the equilibrium condition. 25 cm^3 of the aqueous layer and 10 cm^3 of the non-aqueous layer were withdrawn as the separate portions. Each portion was poured into a 250 cm^3 erlenmayer flask. The concentrations of acetic acid in the aqueous and non-aqueous layers were determined volumetrically against the secondary standard solution of sodium hydroxide.

Similar experiments were carried out with more dilute aqueous acetic acid solutions for 5 different sets of

concentration ranging from 0.1 M to 1 M.　　The experiments described above were performed at 35°C, 25°C and 20°C (except for the system of H_2O/CCl_4 only 32°C was tried). Results of the distribution of acetic acid in two immiscible phases are presented in Tables 3.9, 3.10, 3.11, 3.12 and 3.13.

Table 3.9 The molar concentration of acetic acid in water and benzene at 32°C.

$c_{A(H_2O)}$	$c_{A(benzene)}$	$c_{A(benzene)}/c_{A(H_2O)}$
0.72484	0.01856	0.02561
0.55131	0.01224	0.02220
0.46422	0.00956	0.02059
0.37701	0.00714	0.01894
0.28515	0.00505	0.01771
0.19197	0.00303	0.01578
0.09444	0.00130	0.01376

Table 3.10 The molar concentration of acetic acid in water and carbon tetrachloride at 32°C.

$c_{A(H_2O)}$	$c_{A(CCl_4)}$	$c_{A(CCl_4)}/c_{A(H_2O)}$
0.49702	0.00571	0.01148
0.40228	0.00438	0.01088
0.30300	0.00292	0.00963
0.19892	0.00145	0.00728

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Table 3.11 The molar concentration of acetic acid in water and benzene at 35°C.

$C_{A(H_2O)}$	$C_{A(benzene)}$	$C_{A(benzene)}/C_{A(H_2O)}$
0.48785	0.01125	0.02306
0.38860	0.00827	0.02128
0.29403	0.00567	0.01928
0.21000	0.00383	0.01824
0.09720	0.00142	0.01461

Table 3.12 The molar concentration of acetic acid in water and benzene at 25°C.

$C_{A(H_2O)}$	$C_{A(benzene)}$	$C_{A(benzene)}/C_{A(H_2O)}$
0.47666	0.00960	0.02014
0.37961	0.00683	0.01799
0.28872	0.00398	0.01544
0.19265	0.00255	0.01324
0.09608	0.00117	0.01218

Table 3.13 The molar concentration of acetic acid in water and
benzene at 20°C.

$C_{A(H_2O)}$	$C_{A(benzene)}$	$C_{A(benzene)}/C_{A(H_2O)}$
0.47500	0.00867	0.01825
0.37647	0.00608	0.01618
0.28745	0.00405	0.01409
0.19235	0.00246	0.01280
0.09608	0.00103	0.01072

3.3 The infrared spectroscopic study of aqueous acetic acid

A comparative study on the IR spectra of the solution
of acetic acid in water, benzene and carbon tetrachloride was
carried out using Shimadzu Infrared Spectrophotometer model
IR-440 in conjunction with BaF_2 and ZnSe cells (manufactured
by Pye Unicam, England). The test solutions i.e. acetic acid
in water, acetic acid in benzene and acetic acid in carbon
tetrachloride at various concentrations were prepared by the
standard procedure as described in 3.1.   The corresponding
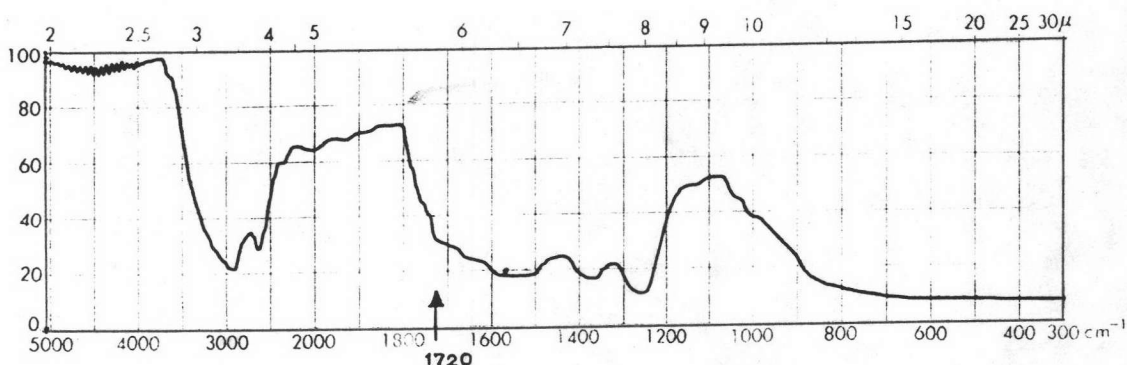spectra are shown in Figs 3.2, 3.3 and 3.4.

Figure 3.2 The IR spectrum of 10 %w/w acetic acid in water
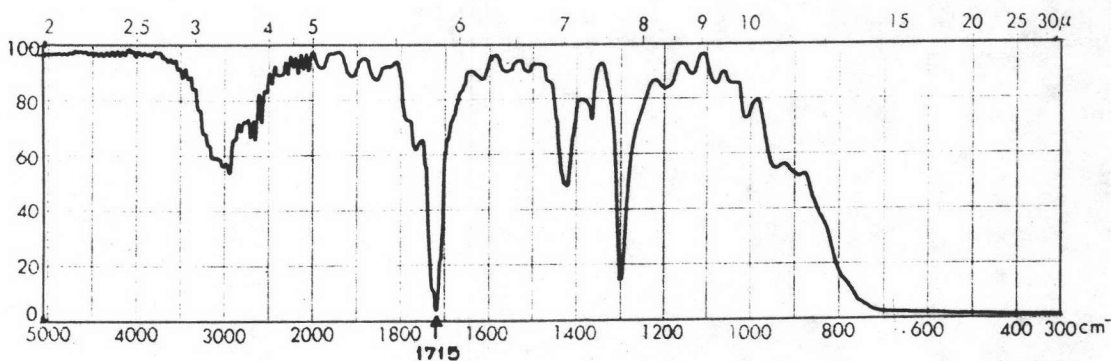shows the combination band at about 1720 cm^{-1}.

Figure 3.3 The IR spectrum of 3 %w/w acetic acid in benzene
shows the band of carbonyl stretching at 1715 cm^{-1} which
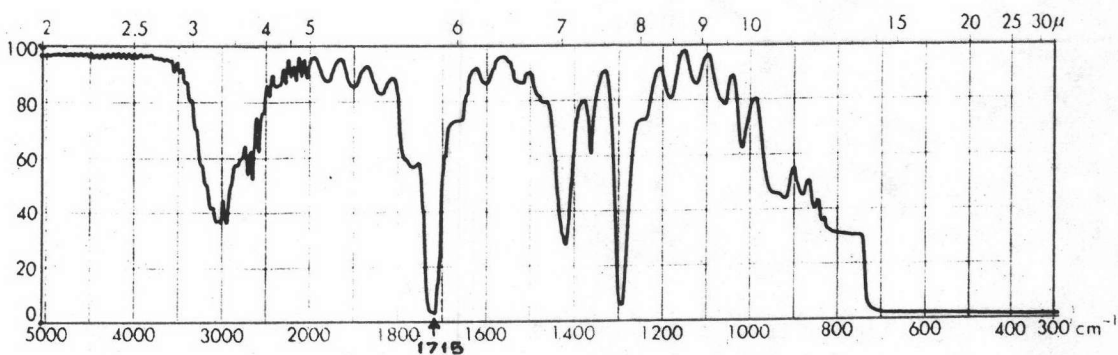indicates the presence of the cyclic dimer species.

Figure 3.4 The IR spectrum of 3 %w/w acetic acid in carbon
tetrachloride shows the band of carbonyl stretching at 1715 cm^{-1}.