

CHAPTER-III

DISCUSSION - PART 1

(CONDUCTANCE STUDIES)

CONDUCTANCE STUDIES IN H₂O + AN MIXTURES AT 25°C

The basic aim of the investigation reported in this dissertation was to study the kinetics of the reversible reaction (1) in H₂O + AN mixtures. It has, however, been thought meaningful to include some basic studies so that the fundamental concepts upon which the kinetics of this reaction is based should be understood. The basis for the kinetics of the reversible reaction (1) is the strong preferential solvation of Cu⁺ by AN in H₂O + AN mixtures. In order to throw some light on the preferential solvation behaviour of Cu⁺ and ClO₄⁻ in H₂O + AN mixtures and to compare the results with those of Parker and coworkers²⁻⁴ obtained using emf and NMR methods, some conductance measurements have also been undertaken in the present investigation. The results of the conductance measurements are reported in this chapter while those of kinetic measurements are given in Chapters IV and V.

Molar conductances of Bu₄NBPh₄, Bu₄NClO₄ and CuClO₄.4AN in AN and in H₂O + AN mixtures containing 93.6, 80.2, 71.6, 58.0 and 46.5 mol % AN have been measured in the concentration range 1-50 x 10⁻⁴ mol dm⁻³ at 25°C. The measured molar conductances (Λ) and the corresponding molar concentrations (C) are reported in TABLES 1 to 3. The physical constants¹⁰² of AN and H₂O + AN mixtures and the corresponding Bjerrum critical distances¹⁰³ have

TABLE 1 contd/...

	<u>71.6% AN</u>												
10^4C	2.830	5.616	11.06	16.33	21.45	26.42							
Δ	94.9	93.3	89.8	87.9	85.8	84.3							
	<u>58.0% AN</u>												
10^4C	1.415	2.808	6.858	11.98	16.80	21.35	25.65						
Δ	82.6	81.2	78.8	76.4	74.8	73.4	72.2						
	<u>46.5% AN</u>												
10^4C	0.849	1.059	2.098	4.115	7.925	11.46	14.76	17.83	20.71	23.40	25.94	28.32	30.57
Δ	72.8	72.4	71.6	69.7	67.5	65.9	65.3	64.4	63.7	63.0	62.4	62.2	61.6

TABLE 2

Molar conductances, Λ ($\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and the corresponding molar concentrations, C (mol dm^{-3})
for Bu_4NClO_4 in AN and in $\text{H}_2\text{O} + \text{AN}$ mixtures at 25°C

		<u>100% AN</u>									
$10^4 C$	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	48.47
Λ	161.5	159.0	156.0	153.7	152.0	150.0	149.0	147.5	146.5	145.5	144.5
		<u>23.6% AN</u>									
$10^4 C$	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	48.47
Λ	154.5	152.2	149.0	146.7	145.0	143.2	141.7	140.05	139.1	138.0	137.0
		<u>80.2% AN</u>									
$10^4 C$	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	
Λ	145.1	143.0	138.2	135.8	133.4	131.3	128.7	127.2	125.6	124.5	

TABLE 2 contd/...

		<u>71.6% AN</u>									
10^4C	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	48.47
Δ	135.4	133.6	130.1	127.6	126.1	124.5	123.2	122.0	121.0	119.8	118.7
		<u>58.0% AN</u>									
10^4C	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	48.47
Δ	125.6	121.7	118.7	116.5	115.1	113.5	112.4	111.6	110.6	110.1	109.5
		<u>46.5% AN</u>									
10^4C	2.789	5.534	10.90	16.09	21.14	26.03	30.78	35.39	39.87	44.23	48.47
Δ	109.1	108.1	106.1	104.5	103.2	102.3	101.5	100.6	100.1	99.5	99.0

TABLE 3

Molar conductances, Λ ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) and the corresponding molar concentrations, C (mol dm^{-3})
for CuClO_4 in AN and in $\text{H}_2\text{O} + \text{AN}$ mixtures at 25°C

	<u>100% AN</u>							
10^4C	11.30	22.27	29.40	39.85	50.01	59.89	72.64	84.94
Λ	154.5	148.6	145.4	140.9	137.5	134.3	131.1	128.1
	<u>23.6% AN</u>							
10^4C	2.912	5.778	11.38	16.81	22.08	27.18		
Λ	155.5	152.8	148.4	146.0	142.6	141.4		
	<u>80.2% AN</u>							
10^4C	2.912	5.778	11.38	16.81	22.07	27.18		
Λ	146.5	144.0	140.2	136.8	135.2	133.2		

TABLE 3 contd./...

		<u>71.6% AN</u>								
^{10}C	2.912	5.778	11.38	16.81	22.07	27.18				
Δ	138.0	135.9	132.1	128.8	127.0	124.8				
		<u>58.0% AN</u>								
^{10}C	2.912	5.778	11.38	16.81	22.07	27.18	32.14	36.96	41.64	46.19
Δ	128.3	126.1	122.6	120.4	119.0	117.2	116.3	115.2	114.2	113.4
		<u>46.5% AN</u>								
^{10}C	2.912	5.778	11.38	16.81	22.07	27.18	32.14	36.96	41.64	46.19
Δ	118.0	115.5	112.3	110.4	108.7	107.7	106.4	105.8	105.0	104.6

been reported in TABLE 4. The limiting molar conductance (Λ_0) and the association constant (K_A) in all the cases have been iteratively calculated by a least squares treatment with IBM-1620 computer using Shedlovsky's method¹⁰⁴⁻¹⁰⁶ involving the following equations:

$$\frac{1}{S\Lambda} = \frac{1}{\Lambda_0} + \frac{C\Lambda S f_{\pm}^2 K_A}{\Lambda_0^2} \quad (5)$$

$$S = \left(\frac{\beta \sqrt{C\Lambda}}{2\Lambda_0^{3/2}} + \sqrt{1 + \frac{\beta^2 C\Lambda}{4\Lambda_0^3}} \right)^2 \quad (6)$$

$$\beta = \frac{8.204 \times 10^5 \Lambda_0}{(DT)^{3/2}} + \frac{82.5}{\eta (DT)^{1/2}} \quad (7)$$

$$\log f_{\pm} = - \frac{1.8246 \times 10^6 \sqrt{C\infty} / (DT)^{3/2}}{1 + 50.29 \times 10^8 R \sqrt{C\infty} / (DT)^{1/2}} \quad (8)$$

$$\text{and } \infty = \frac{S\Lambda}{\Lambda_0} \quad (9)$$

The Λ_0 and K_A values obtained for various electrolytes in AN and in $H_2O + AN$ mixtures are reported in TABLE 5. The dielectric constant (D) and the viscosity (η) for AN and $H_2O + AN$ mixtures for the analysis of the conductance data were taken as reported in TABLE 4.

Justice^{107,108} has suggested that Bjerrum critical distance¹⁰³

$$q = \frac{|z_1 z_2| e^2}{2 D k T} \quad (10)$$

TABLE 4

Dielectric constant^a (D), the viscosity^a (η), the Bjerrum critical distance (q) and the r_y parameter of the Gill equation (14) for AN and H₂O + AN mixtures at 25°C

mol % AN	D	η (cP)	q (Å)	r_y (Å)
100	36.00	0.341	7.79	0.85
93.6	36.89	0.355	7.60	0.87
80.2	39.21	0.387	7.15	0.91
71.6	41.07	0.424	6.83	0.93
58.0	44.53	0.503	6.30	0.97
46.5	48.30	0.597	5.81	1.00

^a D and η values in this TABLE have been taken from Ref.(102).

TABLE 5

Λ_{\circ} ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) and K_A ($\text{dm}^3 \text{mol}^{-1}$) values^a for some electrolytes in AN and in $\text{H}_2\text{O} + \text{AN}$ mixtures at 25°C derived by Shedlovsky's method^b

Electrolyte	Solvent (mol % AN)											
	100		93.6		80.2		71.6		58.0		46.5	
	Λ_{\circ}	K_A	Λ_{\circ}	K_A	Λ_{\circ}	K_A	Λ_{\circ}	K_A	Λ_{\circ}	K_A	Λ_{\circ}	K_A
$\text{Bu}_4\text{NBPPh}_4$	120.0	11	114.6	22	106.5	22	99.4	23	84.8	27	72.7	30
Bu_4NClO_4	165.6	10	160.0	11	150.6	12	139.7	11	127.3	11	111.9	-
CuClO_4	168.0	14	161.5	13	151.8	15	143.2	14	131.4	13	119.9	13

^a Λ_{\circ} and K_A values of this TABLE have maximum uncertainty of $\pm 0.2\%$ and $\pm 10\%$ respectively.

^b K_A values less than 10 were dropped out from this TABLE because these values have no practical significance (Ref. (106)).

should be used for the calculation of the mean ion activity coefficients (f_{\pm}) of the electrolytes from equation (8). This suggestion has been followed by a number of workers¹⁰⁹⁻¹¹¹ and has been confirmed by Gill and Malhotra¹¹² by measuring the activity coefficients of sparingly soluble salts in DMF. The derived conductance parameters reported in TABLE 5 have, thus, been calculated after setting $R = q$, in equation (8). The q values reported in TABLE 4 for AN and $H_2O + AN$ mixtures used were calculated from equation (10). The maximum standard deviations in Λ_o and K_A values of TABLE 5 obtained by applying standard statistical equations¹¹³ were found to be always less than $\pm 0.2\%$ and $\pm 10\%$ respectively.

The root mean square deviations calculated from the standard deviations of the individual points using the relation

$$\sigma_{\Lambda} = \left[\sum (\sigma_{\Lambda}')^2 / (N-2) \right]^{1/2} \quad (11)$$

where N is the number of data points in each conductance set and $\sigma_{\Lambda}' = \Lambda_{cal} - \Lambda_{exp}$, in no case exceeded the experimental uncertainty of the present conductance measurements i.e. $\pm 0.2\%$. This shows a good applicability of Shedlovsky's equation to the present conductance data.

The reproducibility of the present conductance measurements is about $\pm 0.2\%$. Therefore, the use of the 1957-Fuoss-

Onsager^{106,114} conductance equation, the Pitts equation^{115,116}, the Pitts equation arranged in the form of 1957-Fuoss-Onsager equation¹¹⁷, Fuoss-Onsager-Skinner equation¹¹⁸, Fuoss-Hsia equation^{119,120} and its modification¹²¹, the equation proposed by Justice^{108,122} and the other equations of Fuoss¹²³⁻¹²⁵ which demand a precision of the conductance data much better than $\pm 0.1\%$ was not thought appropriate for the analysis of the present conductance data. Moreover, the basic aim of the present studies was not to test the validity of the above mentioned conductance equations but it was to make an investigation of the solvation behaviour of Cu^+ and ClO_4^- in $\text{H}_2\text{O} + \text{AN}$ mixtures, so that some information on the preferential solvation of these ions is available before the kinetics of the reversible reaction (1) are discussed.

To have an indication of the precision of the present conductance measurements, the Λ_0 values for Bu_4NBPh_4 , Bu_4NClO_4 and CuClO_4 equal to 120.0, 165.6 and 168.0 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively in pure AN from TABLE 5 can be well compared with Λ_0 values, 119.7¹²⁶, 165.1¹²⁶ and 168.4¹⁰ $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ respectively, already known in the literature.

LIMITING ION CONDUCTANCES

In order to obtain a better understanding of ion-solvation, an accurate data on the properties of individual ions of the

electrolytes are needed because the cation-solvent and the anion-solvent interactions are different²¹. It is, however, a complicated problem to divide the total parameter of the electrolytes into that of the individual ions.

The limiting molar conductance of an electrolyte at infinite dilution (Λ_0) can be split up into the contribution of individual ions by the use of transport numbers, but transport number measurements are generally laborious and difficult and have not been frequently carried out in mixed solvents. A simple alternative method has been to employ as a reference electrolyte, a tetraalkylammonium salt, the ions of which are equal in size and which do not have solvation effects. The ionic conductances of the two ions in such a case are taken as half of the Λ_0 value of the reference electrolyte^{127,128}. The reference electrolytes often used for this purpose are Bu_4NBPh_4 ¹²⁹, $(i\text{-Amyl})_3\text{BuNBPh}_4$ ¹³⁰, $(i\text{-Amyl})_4\text{NB}(i\text{-Amyl})_4$ ¹²⁶ and Bu_4NBBu_4 ^{32,97} which give limiting ion conductances ($\overset{\circ}{\lambda}_i$) in satisfactory agreement with those obtained from direct transport number measurements in non-aqueous and mixed solvents. Fuoss and coworkers¹³¹⁻¹³³ have used the assumption that the transport number of Bu_4N^+ in Bu_4NBPh_4 is equal to 0.519 and is independent of the nature of the solvent medium. Using this assumption of Fuoss and coworkers¹³¹⁻¹³³ (which is claimed to be valid within $\pm 1\%$), limiting ion conductances $\overset{\circ}{\lambda}_i$ for Bu_4N^+ and Ph_4B^- in AN

and in $H_2O + AN$ mixtures have been calculated from the Λ_0 values of Bu_4NBPh_4 from TABLE 5. From these values and the Λ_0 values of Bu_4NClO_4 and $CuClO_4$ (TABLE 5), limiting ion conductances for ClO_4^- and Cu^+ have been computed by Kohlrausch's law of independent ion conductances. Limiting ion conductances for Bu_4N^+ , Ph_4B^- , ClO_4^- and Cu^+ , thus obtained are reported in TABLE 6.

The validity of the assumption of Fuoss and coworkers can be checked from a comparison of the ion conductances of Bu_4N^+ , Ph_4B^- , ClO_4^- and Cu^+ in pure AN reported in TABLE 6 with such values obtained from direct transference number measurements in AN. The limiting ion conductances 62.3, 57.7, 103.3 and 64.7 $ohm^{-1} cm^2 mol^{-1}$ for these ions in AN in TABLE 6 are within $\pm 1.5\%$ in agreement with the values reported by Springer and coworkers¹³ and Yeager and Kratochvil¹⁰ using direct transference number measurements in AN.

Bu_4NBPh_4 was not soluble in the water-rich region of $H_2O + AN$ mixtures, therefore, the conductance measurements in the present work were attempted only upto 46.5 mol % AN i.e. upto the region in which Bu_4NBPh_4 had sufficient solubility for the conductance measurements.

SOLVATED RADII OF IONS AND PREFERENTIAL SOLVATION

Solvation is understood to mean the interaction between the solute and the solvent. The extent of solvation depends

TABLE 6

Limiting ion conductances, λ_i° ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) and the actual solvated radii, r_i (\AA) for various ions in AN and in $\text{H}_2\text{O} + \text{AN}$ mixtures at 25°C

Ion	Solvent (mol % AN)															
	100	93.6	80.2	71.6	58.0	46.5	10.0	0.00	λ_i°	r_i	λ_i°	r_i				
Bu_4N^+	62.3	5.1	59.5	5.1	55.3	5.1	51.6	5.1	44.0	5.1	37.7	5.1	-	-	19.2 ^a	5.0
Ph_4B^-	57.7	5.4	55.1	5.4	51.2	5.4	47.8	5.4	40.8	5.4	35.0	5.4	-	-	-	-
ClO_4^-	103.3	3.5	100.5	3.5	95.3	3.5	88.1	3.5	83.3	3.4	74.2	3.4	-	-	67.3 ^a	3.4
Cu^+	64.7	5.0	61.0	5.0	56.5	5.0	55.1	4.9	48.1	4.8	45.7	4.5	36.0 ^b	4.2	62.0 ^b	3.3

^a Ref. (135).

^b Taken from Ref. (2).

largely upon the system considered. For inert gases and organic compounds the solvation in a solvent is much smaller than that for the electrolytes in the same solvent. For ionic solutions, the solvation is the measure of ion-solvent interactions which are usually of ion-dipole type except for Ag^+ and Cu^+ where they can be of specific type also^{15,16}.

Various attempts have been made to have an estimate of the stable solvation (primary solvation) formed around the ions in aqueous solutions¹³⁶. The simple and accurate method for estimating primary solvation number is based on Robinson-Stokes¹³⁶ model of solvation which rests upon determining the radius of the solvated ion by measuring the rate of migration of the ion against the viscous drag of the solvent, i.e. by the use of ionic conductances. According to Robinson-Stokes' law¹³⁶ the radius of the solvated ion (r_s) is given by equation (12):

$$r_s = \left| z \right| F^2 / 6 \pi \eta N \lambda_{\pm}^{\circ} = 0.82 \left| z \right| / \eta \lambda_{\pm}^{\circ} \quad (12)$$

where the letters have the usual significance¹³⁶.

The study of solvation of ions in non-aqueous and mixed solvents has been more or less neglected for a long time due to the inapplicability of the Robinson-Stokes' equation (12) to the ions of common dimensions. The problem, however, has attracted the attention of some workers during the last few years. They

have incorporated the corrections suggested by Robinson and Stokes for the applicability of their law to the tetraalkylammonium^{23,137,138} ions. Tetraalkylammonium ions are assumed to be unsolvated due to their large size and small surface charge density and, hence, are supposed to interact very little with the solvent molecules¹³⁶. The classical Stokes' law is accepted to apply to these ions. The r_s value calculated from equation (12) for each tetraalkylammonium ion turns out to be smaller than the respective crystallographic radius (r_c) of the ion in question. One would, however, expect r_s in equation (12) to be equal to r_c , since the ion is unsolvated. Clearly a correction factor in equation (12) and that of the classical Stokes' law from which it is obtained need to be applied in order that equation (12) may provide the values of r_s for the tetraalkylammonium ions equal to their crystallographic radii.

In order to apply a correction to the solvated radii of the ions, Robinson and Stokes constructed a calibration curve by plotting r_c/r_s versus r_s for the tetraalkylammonium ions in aqueous solutions¹³⁶. From the plot, the correction factor (r_c/r_s) for the various ions of common ionic dimensions for which r_s was calculated from equation (12) were read off. Thus the corrected radius (r_{cor}) of the solvated ions for which Robinson-Stokes' law is non-applicable without correction were given by equation (13):

$$r_{cor} = \frac{0.82 |z|}{\eta \lambda_{\pm}^{\circ}} \cdot \left(r_c / r_s \right) \quad (13)$$

Nightingale¹³⁹ discussed the limitations of Robinson-Stokes' calibration curve and introduced a new method for the evaluation of corrected solvated radii of various ions directly by plotting r_c versus r_s for the tetraalkylammonium ions in aqueous solutions and then reading off the corrected radii of the solvated ions directly corresponding to the r_s values of the ions.

Recently an empirical equation has been proposed by Gill^{140,141} from which the actual solvated radii of ions in non-aqueous and mixed solvents can be directly calculated. This equation can be written as:

$$r_i = \left| Z \right| F^2 / (6 \pi N \eta \lambda_i^{\circ}) + 0.0103D + r_y \quad (14)$$

where r_i is the actual solvated radii of the ion, D is the static dielectric constant of the medium and r_y is a constant factor.

In the Gill equation^{140,141} r_y value for the unassociated solvents is to be selected as 0.85 Å and for the associated and hydrogen-bonded solvents equal to 1.13 Å. In binary solvent mixtures of two dipolar aprotic solvents where no solvent association occurs r_y value is also to be selected equal to 0.85 Å^{142,143}. In binary solvent mixtures of dipolar aprotic + dipolar protic solvents, however, where the solvent association is small but not negligible, r_y value at a particular solvent

composition in the mixture can be computed by assuming that r_y value varies linearly between 0.85 and 1.13 Å i.e. from the unassociated solvent to the associated or hydrogen-bonded solvent with the solvent composition varying from one pure solvent to the other. Following this assumption, r_y values for the Gill equation (14) in various H₂O + AN mixtures have been computed from the linear plot of r_y between 0.85 and 1.13 Å corresponding to AN composition varying from 100 to 0 mol %. The r_y values thus obtained for H₂O + AN mixtures are reported in TABLE 4 alongwith other physical properties of these solvent mixtures.

Using equation (14), the λ_i° values for various ions from TABLE 6 and the r_y values as reported in TABLE 4, the r_i values for Bu₄N⁺, Ph₄B⁻, ClO₄⁻ and Cu⁺ in AN and in H₂O + AN mixtures have been calculated and are also reported in TABLE 6.

Conductance measurements reported in the present work could not provide λ_i° values for various ions in the water-rich region of H₂O + AN mixtures because the conductance measurements were made only upto 46.5 mol % AN. In pure water and in H₂O + AN mixtures rich with water, λ_i° values for Cu⁺ were taken from the work reported by Parker and coworkers² so that information regarding solvation of this cation over the entire solvent composition range of the solvent mixtures could be obtained. Therefore, λ_i° values for Cu⁺ in water and in H₂O + AN mixtures containing 10 mol % AN were taken from Ref. (2) and such values

for Bu_4N^+ and ClO_4^- in pure water were taken from Ref. (135). The λ_c° values in water and in $\text{H}_2\text{O} + \text{AN}$ mixture containing 10 mol % AN so obtained alongwith the corresponding r_i values have also been reported in TABLE 6.

A perusal of the r_i values of TABLE 6 shows that these values for Bu_4N^+ and Ph_4B^- in $\text{H}_2\text{O} + \text{AN}$ mixtures remain constant and equal to the corresponding crystallographic radii ($\text{Bu}_4\text{N}^+ = 5.00$ and $\text{Ph}_4\text{B}^- = 5.35 \text{ \AA}$)^{126,142}. The variation of r_i value for Cu^+ with solvent composition shows an interesting behaviour. The r_i value for Cu^+ increases non-linearly from pure water to ≈ 80 mol % AN in $\text{H}_2\text{O} + \text{AN}$ mixtures and then becomes constant and equal to the value in pure AN. This shows that the solvation of Cu^+ increases from pure water upto ≈ 80 mol % AN and beyond this solvent composition when the solvation sphere of this cation becomes complete, no further increase in solvation takes place. Studies of Parker and coworkers² show that Cu^+ forms $[\text{Cu}(\text{AN})_2]^+$, $[\text{Cu}(\text{AN})_3]^+$ and $[\text{Cu}(\text{AN})_4]^+$ complexes in $\text{H}_2\text{O} + \text{AN}$ mixtures. When AN content in the mixture is small, more frequently formed complex is $[\text{Cu}(\text{AN})_2]^+$ and in AN-rich region $[\text{Cu}(\text{AN})_4]^+$ complex is mostly formed. Thus, the increase in the solvation of Cu^+ with the increase of AN in $\text{H}_2\text{O} + \text{AN}$ mixtures continues till $[\text{Cu}(\text{AN})_2]^+$ complex changes into $[\text{Cu}(\text{AN})_4]^+$ complex through $[\text{Cu}(\text{AN})_3]^+$ complex. When $[\text{Cu}(\text{AN})_4]^+$ complex formation is complete at ≈ 80 mol % AN, no further increase in the solvation and hence

in the r_1 value takes place. These results show a strong preferential solvation of Cu^+ by AN in $\text{H}_2\text{O} + \text{AN}$ mixtures over the entire solvent composition range. The free energy of transfer of Cu^+ from water to $\text{H}_2\text{O} + \text{AN}$ mixtures reported by Parker and coworkers^{4,144} over the whole solvent composition range also shows exactly similar trend and confirm these results.

The r_1 value for ClO_4^- , on the other hand, shows that this value over the entire solvent composition range remains practically constant indicating thereby that ClO_4^- is not preferentially solvated by any of these solvents. Parker and coworkers¹⁵ have reported the free energy of transfer for ClO_4^- from water to AN equal to $1.1 \text{ Kcals mol}^{-1}$ which indicates a small amount of preferential hydration of ClO_4^- . This value of the free energy of transfer for ClO_4^- from water to AN, however, is very small, and because of large uncertainties in its evaluation, can not be reliably taken to indicate preferential hydration of ClO_4^- . In conclusion, these conductance studies show that Cu^+ is strongly preferentially solvated by AN over the entire composition range of $\text{H}_2\text{O} + \text{AN}$ mixtures.