

## CHAPTER -IX

### STUDY ON INTERACTIONS OF SOME METAL PERCHLORATES PREVAILING IN FORMAMIDE BY PHYSICO-CHEMICAL APPROACH

#### 9.1. Introduction

Physicochemical study on the transport properties of electrolytes has been utilized to investigate the solvation and association behavior of ions in different solvent media. Electrolytic concentration and viscosity of the solvent plays a vital part in deciding the electrical conductivity in solvents.

Perchlorates are the high melting point inorganic salts easily soluble in water and protic solvents. One of the most promising potential applications of lithium perchlorate is in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [1]. Sodium perchlorate can be used to block iodine uptake for the patients with subclinical hyperthyroidism [2].

Study of Conductance has been employed to measure association and behavior of ions in solution. Techniques such as volumetric, viscometric and interferometric studies help to investigate the molecular interactions in solution and to inspect the activities of the salt with different solvent concentrations. Study of apparent and limiting apparent molar volumes of the electrolyte along with the dependence of viscosity on the concentration of salt have been demonstrated as a function of ion-ion and ion-solvent interactions [3]. In conjunction with our investigation on electrical conductance of electrolytes [4-6] the present work deals with the transport and thermodynamic properties of Lithium Perchlorate, Sodium Perchlorate and Potassium Perchlorate in Formamide at 298.15 K.

#### 9.2. Experimental Methods

##### 9.2.1. Source and Purity of the Sample

$\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  of puriss grade were obtained from Aldrich, Germany and used as purchased. Formamide of spectroscopy grade was procured from Sd. fine Chemicals. Standard methods [7] were applied for the purification of the solvent.

### 9.2.2 Apparatus and Procedure

A stock solution for each salt was prepared by mass and the working solutions were obtained by mass dilution at 298.15K. The conversion of molarity to molality was done using density values. The uncertainty of molarity of different solutions is found to be  $\pm 0.0001 \text{ mol dm}^{-3}$ . The density ( $\rho$ ) was measured by a vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of  $0.0005 \text{ g/cm}^3$ . The calibration was done by double-distilled water and dry air and uncertainty in density was  $\pm 0.00005 \text{ g cm}^{-3}$ .

Solvent viscosities were measured by means of a suspended Ubbelohde-type viscometer being calibrated at 298.15 K with doubly distilled water and purified methanol using density and viscosity values from the literature [8-10]. A perfectly dried and thoroughly cleaned viscometer filled with experimental solution was placed vertically in the glass-walled thermostat (Bose Panda Instruments Pvt. Ltd.) maintained to  $\pm 0.01 \text{ K}$ . After attainment of thermal equilibrium, efflux times of flow were recorded with a stopwatch correct to  $\pm 0.1 \text{ s}$ . At least three repetitions of each data reproducible to  $\pm 0.1 \text{ s}$  were taken to average the flow times. Viscosity of the solution,  $\eta$  can be determined using the following equation:

$$\eta = (Kt - L/t)\rho \quad (1)$$

where  $K$  and  $L$  are the viscometer constants and  $t$  and  $\rho$  are the efflux time of flow in seconds and the density of the experimental liquid respectively. The uncertainty in viscosity measurements is within  $\pm 0.003 \text{ mPas}$ .

Conductance measurements were performed in a Systronic-308 conductivity bridge (accuracy  $\pm 0.01 \%$ ) using a dip-type immersion conductivity cell, CD-10, having a cell constant of approximately ( $0.1 \pm 0.001$ ). A water bath maintained within  $T = (298.15 \pm 0.01) \text{ K}$  was used and the cell was calibrated by the method proposed by Lind et al [11]. The conductance data were reported at a frequency of  $1 \text{ kHz}$  and were uncertain to  $\pm 0.3 \%$ .

Speeds of sound were recorded by multifrequency ultrasonic interferometer (Mittal Enterprise, New Delhi) working at 1 MHz with a precision of 0.2 m.s<sup>-1</sup>. Its calibration was carried out with three solvents namely water, methanol, and benzene at 298.15 K. The full details of the methods and techniques have been revealed earlier [12-14]. The uncertainty of ultrasonic speed measurements was  $\pm 0.2$  m.s<sup>-1</sup>. The uncertainty for the working temperature was  $\pm 0.02$  K.

### 9.3. Result and Discussion

The experimental values of physical properties of the pure solvent were in good agreement with those found in the literature, as in Table 1. The values of equivalent conductances ( $\Lambda$ ) at various concentrations are exhibited in Table 2 and the conductance data for LiClO<sub>4</sub>, NaClO<sub>4</sub> and KClO<sub>4</sub> in Formamide have been examined with the help of the Fuoss conductance equation [15,16]. The limiting molar conductance ( $\Lambda_0$ ), the association constant ( $K_A$ ) and the distance of closest approach of ions ( $R$ ) are derived for a given set of conductivity values ( $c_j, \Lambda_j, j=1, \dots, n$ ) from the following set of equations.

$$\Lambda = P\Lambda_0[(1+R_X) + E_L] \quad (2)$$

$$P = 1 - \alpha(1 - \gamma) \quad (3)$$

$$\gamma = 1 - K_A c \gamma^2 f^2 \quad (4)$$

$$-\ln f = \beta \kappa / 2(1 + \kappa R) \quad (5)$$

$$\beta = e^2 / (\epsilon k_B T) \quad (6)$$

$$K_A = K_R / (1 - \alpha) = K_R / (1 + K_S) \quad (7)$$

where the relaxation field effect is denoted by  $R_X$ ,  $E_L$  corresponds to the electrophoretic counter current,  $k^{-1}$  denotes the radius of the ion atmosphere,  $e$  is the electron charge,  $\epsilon$  is the relative permittivity of the solvent mixture,  $k_B$  is the Boltzmann constant,  $c$  is the molarity of the solution,  $K_A$  is the overall pairing constant,  $K_R$  is the association constant of the solvent-separated pairs,  $K_S$  is the association constant of the contact-pairs,  $\gamma$  is the fraction of solute present as unpaired ion,  $\alpha$  is the fraction of contact pairs,  $\beta$  is twice the Bjerrum distance,  $f$  is the activity coefficient and  $T$  is the absolute temperature. The computations were performed by dint of using a

program suggested by Fuoss. Shedlovsky extrapolation [17] of the data were used to obtain the initial  $\Lambda_0$  values for the iteration procedure. Input for the program is the set  $(c_j, \Lambda_j, j=1, \dots, n), n, \varepsilon, \eta, T$ , initial values of  $\Lambda_0$ , and an instruction to cover a pre-selected range of  $R$  values.

For the minimization of standard deviation all the calculations are performed by finding the values of  $\Lambda_0$  and  $\alpha$ .

$$\delta^2 = \sum [A_j(cal) - A_j(obs)]^2 / (n-2) \quad (8)$$

For a sequence of  $R$  values and then plotting  $\delta$  against  $R$ , the minimum of the  $\delta$  versus  $R$  curve represents the best-fit  $R$ . Hence, approximate runs are carried out over a fairly wide range of  $R$  values using 0.1 increments for the location of the minimum, but no significant minima were found in the  $\delta$ - $R$  curves for  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$ , in Formamide;  $R$  values are assumed to be  $R = (a + d)$ , where the sum of the crystallographic radii of the ions is represented by  $a$  and the average distance corresponding to the side of a cell occupied by a solvent molecule is designated by  $d$ . This distance  $d$  is given by

$$d (\text{\AA}) = 1.183(M / \rho)^{1/3} \quad (9)$$

where  $M$  is the molar mass of the solvent and  $\rho$  is its density. The values of  $\Lambda_0$ ,  $K_A$ , and  $R$  attained by this procedure are reported in Table 3.

Inspection of Table 3 reveals that the limiting molar conductance  $\Lambda_0$  is found to have an increasing order whilst moving from  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  followed by  $\text{KClO}_4$ . It also implies that the association in Formamide is highest for  $\text{LiClO}_4$  and lowest for  $\text{KClO}_4$  and intermediate in the case of  $\text{NaClO}_4$ . Hence the ion-solvent interaction in Formamide is maximum in the case of  $\text{LiClO}_4$  and minimum for  $\text{KClO}_4$ . The ion-solvent interaction of  $\text{NaClO}_4$  exists between  $\text{LiClO}_4$  and  $\text{KClO}_4$ . This indicates that lowering of conductance of  $\text{KClO}_4$  is found to be highest and least for  $\text{LiClO}_4$ . The lowest viscosity of Formamide for  $\text{KClO}_4$  also supports the above observation because with lowering of viscosity the  $\Lambda_0$  value should increase [18].

The above trend in  $\Lambda_0$  values can be verified through a characteristic function called the Walden product,  $\Lambda_0 \eta$  given in Table 4. Even though the

viscosity of Formamide for  $\text{LiClO}_4$  is more than that of  $\text{NaClO}_4$  and  $\text{KClO}_4$ , the  $\Lambda_0 \eta$  is found to attain an increasing order from  $\text{LiClO}_4$  to  $\text{KClO}_4$  which points out the predominance of  $\Lambda_0$  over  $\eta$ .

$\Delta G^\circ$  is given by the following relationship [19] and is given in Table 4.

$$\Delta G^\circ = -RT \ln K_A \quad (10)$$

The explanation of negative values of  $\Delta G^\circ$  can be given considering the participation of specific covalent interaction in the ion-association process. The decrease in the value of  $\Delta G^\circ$  in formamide for  $\text{LiClO}_4$  than  $\text{KClO}_4$  indicates the highest degree of association in  $\text{LiClO}_4$ . High  $K_A$  values indicate strong ion-association in the media. The ion-association process is exothermic. As a result Gibbs Free Energy change is negative and the ion-association becomes favourable.

The experimental value of densities of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide, as a function of concentration at 298.15K is listed in Table 5. Limiting apparent molar volume is essential to study the interactions of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in the pure solvent. The apparent molar volumes  $\phi_V$  given in Table 5 were obtained from the solution densities using the following equation

$$\phi_V = M / \rho - (\rho - \rho_o) / c \rho \rho_o \quad (11)$$

where  $M$  is the molar mass of the solute,  $c$  is the molarity of the solution,  $\rho$  and  $\rho_o$  are the densities of the solution and pure solvent, respectively. The limiting apparent molar volumes  $\phi_V^0$  were evaluated in accordance with a least-squares treatment to the plots of  $\phi_V$  versus  $\sqrt{c}$  using the following Masson equation [20]

$$\phi_V = \phi_V^0 + S_V^* \cdot \sqrt{c} \quad (12)$$

where  $\phi_V^0$  is the limiting apparent molar volume at infinite dilution and  $S_V^*$  is the experimental slope.

The plots of  $\phi_V$  against the square root of the molar concentration  $\sqrt{c}$  were found to be linear with negative slopes which are shown in Figure 1.

The values of  $\phi_V^0$  and  $S_V^*$  along with the standard errors are reported in Table 5. The extent of ion-solvent interaction can be examined by taking the  $\phi_V^0$  values. A perusal of Table 5 indicates that the  $\phi_V^0$  values are positive and is highest in case of LiClO<sub>4</sub> in Formamide. This indicates that maximum ion-solvent interaction in Formamide is found in the case of LiClO<sub>4</sub> and the same is minimum for KClO<sub>4</sub>. The said interaction of NaClO<sub>4</sub> becomes in between LiClO<sub>4</sub> and KClO<sub>4</sub>. These effects are further represented in the scheme 1 where I<sub>1</sub>, I<sub>2</sub> and I<sub>3</sub> are the extent of ion-solvent interaction of KClO<sub>4</sub>, NaClO<sub>4</sub> and LiClO<sub>4</sub> in Formamide respectively shown in **Scheme 1**. Li<sup>+</sup> ion with highest charge density and smallest in size compared to Na<sup>+</sup> and K<sup>+</sup> favours the accessibility towards formamide rendering the highest ion solvent interaction exhibited by the following scheme. So the interaction of Formamide with Li<sup>+</sup> ion is maximum for LiClO<sub>4</sub> and minimum in the case of K<sup>+</sup> in KClO<sub>4</sub>.

On the other hand, the  $S_V^*$  indicates the extent of ion-ion interaction. The  $S_V^*$  values are negative due to the disappearance of ion-ion attractive force at infinite dilution. The ion-ion interactions decrease with dilution which can be attributed to increase in distance between ions at infinite dilution. The values of  $S_V^*$  shows that the extent of ion-ion interaction in Formamide is maximum for KClO<sub>4</sub> and minimum for LiClO<sub>4</sub>. From the comparison of the magnitude of  $\phi_V^0$  values with that of  $S_V^*$ , it is evident that ion-solvent interactions predominate over ion-ion interactions in all the solutions. Furthermore, the values of  $\phi_V^0$  lead to the fact that the lowest ion-solvent interaction of KClO<sub>4</sub> results in higher conductance than NaClO<sub>4</sub> whereas NaClO<sub>4</sub> exhibits higher conductance than LiClO<sub>4</sub> in Formamide. The viscosity data has been examined using Jones-Dole equation [21]

$$(\eta/\eta_0 - 1)/\sqrt{c} = A + B\sqrt{c} \quad (13)$$

where  $\eta$  and  $\eta_0$  are the viscosities of the solution and solvent respectively. The values of  $A$  and  $B$  are acquired by a computerised least-square method

and recorded in Table 6. This can be achieved from the straight line by plotting  $(\eta/\eta_0 - 1)/\sqrt{c}$  against  $\sqrt{c}$  as depicted in Figure 2.

A perusal of Table 6 reveals the negative values of  $A$  coefficient are generally negative for all of the solutions under investigation and point towards weak ion-ion interactions. The viscosity  $B$  coefficient [22] describes the effects of ion-solvent interactions. Positive values of the viscosity  $B$  coefficients for  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide reflects the presence of strong ion-solvent interactions. The viscosity  $B$ -coefficient value is found to be lowest for  $\text{KClO}_4$  supporting the fact that the conductance is highest  $\text{KClO}_4$ .

The adiabatic compressibility ( $\beta_s$ ) was calculated from the following equation:

$$\beta_s = 1/u^2 \rho \quad (15)$$

where  $u$  is the speed of sound in the solution and  $\rho$  is the density of solution. The apparent molar adiabatic compressibility ( $\phi_K$ ) of the solutions was found out from the relation,

$$\phi_K = M \beta_s / \rho + (\beta_s \rho_o - \beta_o \rho) / c \rho \rho_o \quad (16)$$

where  $\beta_s, \beta_o$  are the adiabatic compressibilities of the solution and solvent respectively and  $c$  is the molarity of the solution. Limiting apparent molar adiabatic compressibilities ( $\phi_K^0$ ) and experimental slopes ( $S_K^*$ ) were achieved by fitting  $\phi_K$  against the square root of molarity ( $\sqrt{c}$ ) of the electrolyte employing the method of least squares.

$$\phi_K = \phi_K^0 + S_K^* \cdot \sqrt{c} \quad (17)$$

The values of  $\beta_s$  and  $\phi_K$  are recorded in Table 7. Since the values of  $\phi_K^0$  and  $S_K^*$  are the measure of ion-solvent and ion-ion interactions respectively, a perusal of Table 7 and Figure 3 reveals that the values are in agreement with results drawn from the values of  $\phi_V^0$  and  $S_V^*$  discussed earlier.

#### 9.4. Conclusion

Extensive investigation of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide reveals that  $\text{LiClO}_4$  is more associated in Formamide than the other two perchlorates and it remains as ion-pairs. The ion-association is found minimum in the case of  $\text{KClO}_4$  in Formamide. The said interaction of  $\text{NaClO}_4$  becomes in between  $\text{LiClO}_4$  and  $\text{KClO}_4$ . The volumetric, viscometric and interferometric studies reveal the predominance of ion-solvent interaction over the ion-ion interaction in all the studied solutions.

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**Table 1** Density ( $\rho$ ), viscosity ( $\eta$ ) and dielectric constant ( $\epsilon$ ) of pure Formamide at 298.15K.

Solute	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta (\text{mPa. s.})$		$u (\text{ms}^{-1})$		$\epsilon$
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
Formamide	1.12908	1.1291[23]	3.299	3.302[23]	1596.1	1597.8[24]	111.0

**Table 2** The concentration ( $c$ ) and molar conductance ( $\Lambda$ ) of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide at 298.15 K.

$c \times 10^4$ (mol.dm <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol.dm <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )	$c \times 10^4$ (mol.dm <sup>-3</sup> )	$\Lambda \times 10^4$ (S. m <sup>2</sup> . mol <sup>-1</sup> )
$\text{LiClO}_4$		$\text{NaClO}_4$		$\text{KClO}_4$	
1.3363	10.31	1.9825	12.38	5.0535	13.05
1.5725	10.16	2.7456	12.24	5.9000	12.85
1.9349	9.98	3.4040	12.01	6.8069	12.76
2.1815	9.88	3.9760	11.73	7.4966	12.56
2.4555	9.75	4.6010	11.53	7.9017	12.45
2.6830	9.64	5.0940	11.35	8.4042	12.38
2.9173	9.51	5.6882	11.23	8.8506	12.36
3.2005	9.37	6.5331	10.98	9.6783	12.14
3.4077	9.27	7.1770	10.86	10.3362	12.08
3.7288	9.10	7.7451	10.62	10.9362	12.01
3.9323	8.99	8.0770	10.64	11.8267	11.79
4.2230	8.85	8.4390	10.53	12.5670	11.73
4.5199	8.72	8.9820	10.31	13.3079	11.51
4.7263	8.63	9.6970	10.16	13.7789	11.44

**Table 3** Limiting molar conductivity ( $\Lambda^0$ ), association constant ( $K_A$ ), co-sphere diameter ( $R$ ) and standard deviations ( $\delta$ ) of experimental  $\Lambda$  of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  at 298.15 K.

Salts	Solvent	$\Lambda^0$ ( $\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$ )	$K_A$ ( $\text{dm}^3\cdot\text{mol}^{-1}$ )	$R$ ( $\text{\AA}$ )	$\delta$
$\text{LiClO}_4$		11.529	921.322	7.6262	5.294
$\text{NaClO}_4$	Formamide	13.533	446.743	7.9561	6.168
$\text{KClO}_4$		14.567	248.296	8.3161	4.895

**Table 4** Walden product ( $\Lambda_0\eta_0$ ) and Gibb's energy change ( $\Delta G^\circ$ ) of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide at 298.15 K.

Solute	$\Lambda_0\eta_0$ ( $\text{Sm}^2\text{mol}^{-1}$ mPas. s.)	$\Delta G^\circ \times 10^{-4}$ ( $\text{J mol}^{-1}$ )
$\text{LiClO}_4$	38.034	-1.6939
$\text{NaClO}_4$	44.645	-1.5125
$\text{KClO}_4$	48.056	-1.3669

**Table 5** Experimental values of densities ( $\rho$ ), apparent molar volume( $\phi_v$ ), limiting apparent molar volume ( $\phi_v^0$ ) and experimental slope ( $S_v^*$ ) of LiClO<sub>4</sub>, NaClO<sub>4</sub> and KClO<sub>4</sub> in Formamide at 298.15 K.

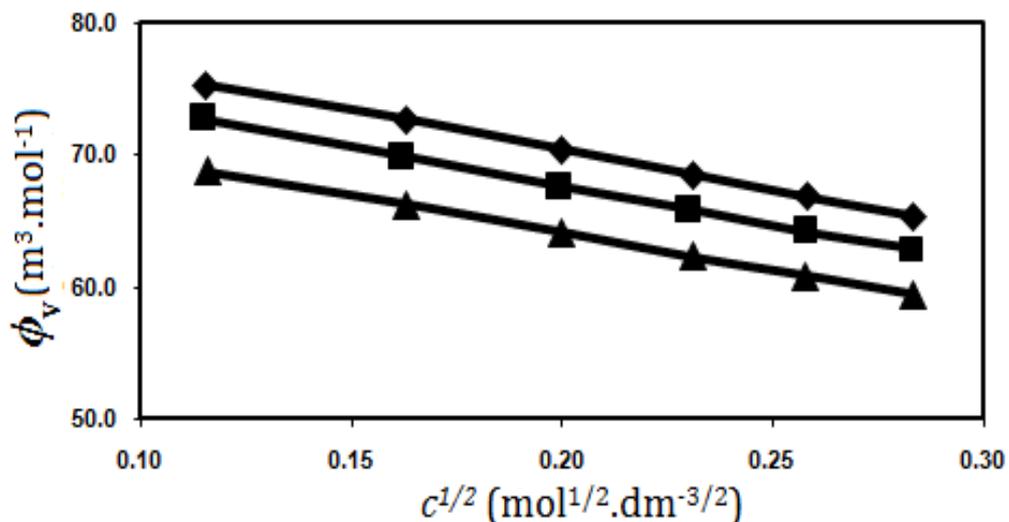
$c$ (mol.dm <sup>-3</sup> )	$\rho \times 10^{-3}$ (kg m <sup>-3</sup> )	$\phi_v \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> )	$\phi_v^0 \times 10^6$ (m <sup>3</sup> . mol <sup>-1</sup> )	$S_v^* \times 10^6$ (m <sup>3</sup> mol <sup>-3/2</sup> kg <sup>1/2</sup> )
LiClO <sub>4</sub> in Formamide				
0.0133	1.12940	75.33272		
0.0265	1.12981	72.67569		
0.0398	1.13029	70.41229	82.3	-59.68
0.0532	1.13082	68.54253		
0.0665	1.13140	66.83022		
0.0799	1.13201	65.39346		
NaClO <sub>4</sub> in Formamide				
0.0132	1.12968	72.7480		
0.0263	1.13037	69.8869		
0.0397	1.13114	67.6158	79.42	-58.74
0.0529	1.13194	65.8661		
0.0663	1.1328	64.2178		
0.0798	1.13368	62.9683		
KClO <sub>4</sub> in Formamide				
0.0134	1.13000	68.7985		
0.0266	1.13099	66.2733		
0.0399	1.13205	64.1524	75.39	-56.46
0.0533	1.13317	62.2918		
0.0665	1.13430	60.8549		
0.0801	1.13551	59.4029		

**Table 6** Experimental values of concentration ( $c$ ), viscosity ( $\eta$ ),  $(\eta/\eta_0-1)/c^{1/2}$ , viscosity A,B- coefficients of LiClO<sub>4</sub>, NaClO<sub>4</sub> and KClO<sub>4</sub> in Formamide at 298.15 K

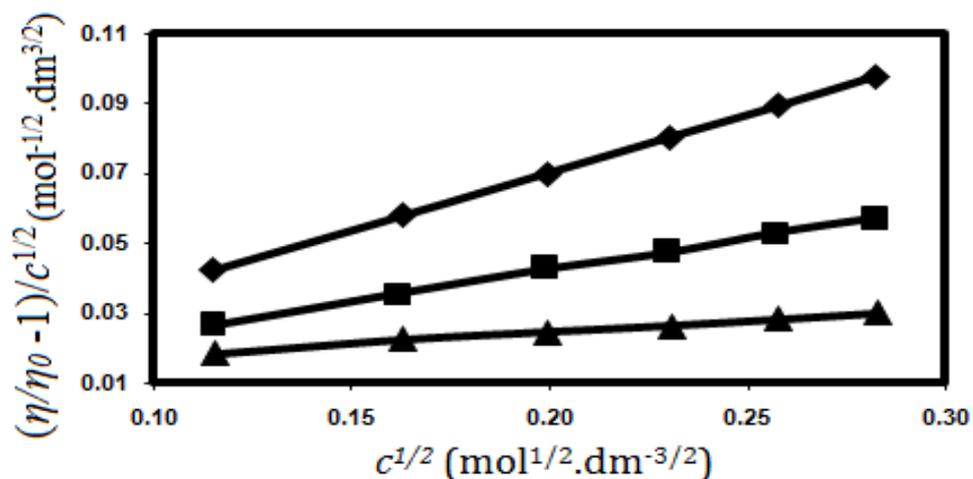
$c$ (mol dm <sup>-3</sup> )	$\eta$ (mPa s)	$(\eta/\eta_0-1)/c^{1/2}$ (kg <sup>1/2</sup> mol <sup>-1/2</sup> )	A (kg. mol <sup>-1</sup> )	B (kg <sup>1/2</sup> mol <sup>-1/2</sup> )
LiClO <sub>4</sub> in Formamide				
0.0133	3.315	0.042	0.003	0.331
0.0265	3.330	0.058		
0.0398	3.345	0.070		
0.0532	3.360	0.080		
0.0665	3.375	0.089		
0.0799	3.390	0.098		
NaClO <sub>4</sub> in Formamide				
0.0132	3.309	0.026	0.005	0.182
0.0263	3.318	0.036		
0.0397	3.327	0.043		
0.0529	3.335	0.047		
0.0663	3.344	0.053		
0.0798	3.352	0.057		
KClO <sub>4</sub> in Formamide				
0.0134	3.306	0.018	0.010	0.067
0.0266	3.311	0.022		
0.0399	3.315	0.024		
0.0533	3.319	0.026		
0.0665	3.323	0.028		
0.0801	3.327	0.030		

**Table 7** Experimental values of speed of sound ( $u$ ), adiabatic compressibility ( $\beta_s$ ) and apparent molar adiabatic compressibility ( $\phi_K$ ), limiting apparent molar adiabatic compressibility ( $\phi_K^0$ ), and experimental slopes ( $S_K^*$ ) of  $\text{LiClO}_4$ ,  $\text{NaClO}_4$  and  $\text{KClO}_4$  in Formamide at 298.15 K.

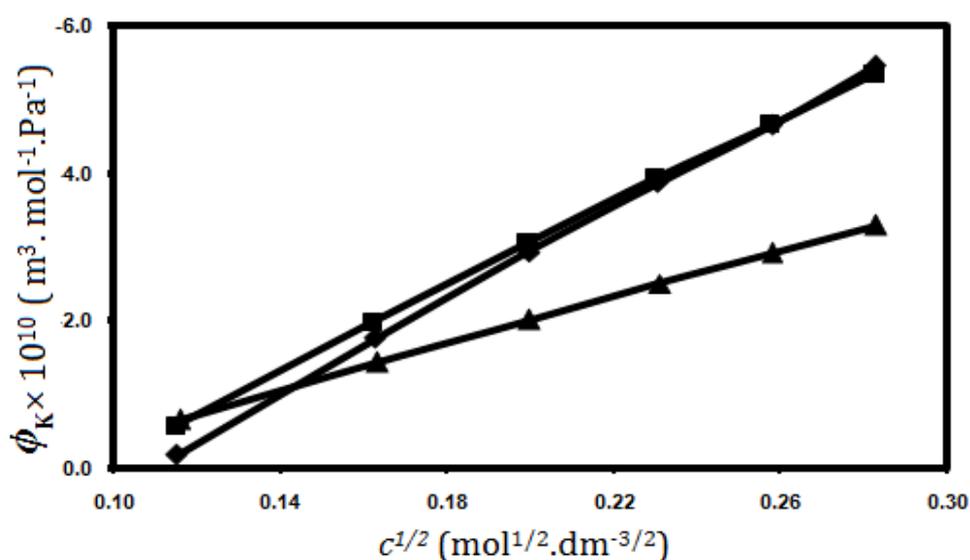
$c$ (mol $\text{dm}^{-3}$ )	$u$ ( $\text{m s}^{-1}$ )	$\beta_s \times 10^{10}$ ( $\text{Pa}^{-1}$ )	$\phi_K \times 10^{10}$ ( $\text{m}^3 \text{ mol}^{-1}$ $\text{Pa}^{-1}$ )	$\phi_K^0 \times 10^{10}$ ( $\text{m}^3 \text{ mol}^{-1}$ $\text{Pa}^{-1}$ )	$S_K^* \times 10^{10}$ ( $\text{m}^3 \text{ mol}^{-3/2}$ $\text{Pa}^{-1} \text{ kg}^{1/2}$ )
LiClO <sub>4</sub> in Formamide					
0.0133	1596.1	3.4766	-0.174		
0.0265	1600.2	3.4578	-1.751		
0.0398	1612.4	3.4045	-2.926		
0.0532	1631.9	3.3222	-3.869	3.372	-31.26
0.0665	1657.5	3.2188	-4.642		
0.0799	1688.5	3.1001	-5.449		
NaClO <sub>4</sub> in Formamide					
0.0132	1601.3	3.4764	-0.561		
0.0263	1613.3	3.4522	-1.963		
0.0397	1632.4	3.3989	-3.048		
0.0529	1657.2	3.3176	-3.932	2.665	-28.46
0.0663	1687.1	3.2168	-4.648		
0.0798	1724.1	3.1014	-5.328		
KClO <sub>4</sub> in Formamide					
0.0134	1601.4	3.4508	-2.567		
0.0266	1609.2	3.4145	-9.320		
0.0399	1620.4	3.3643	-14.833		
0.0533	1634.9	3.3016	-19.531	1.148	-15.74
0.0665	1651.9	3.2308	-23.329		
0.0801	1672.1	3.1498	-26.924		



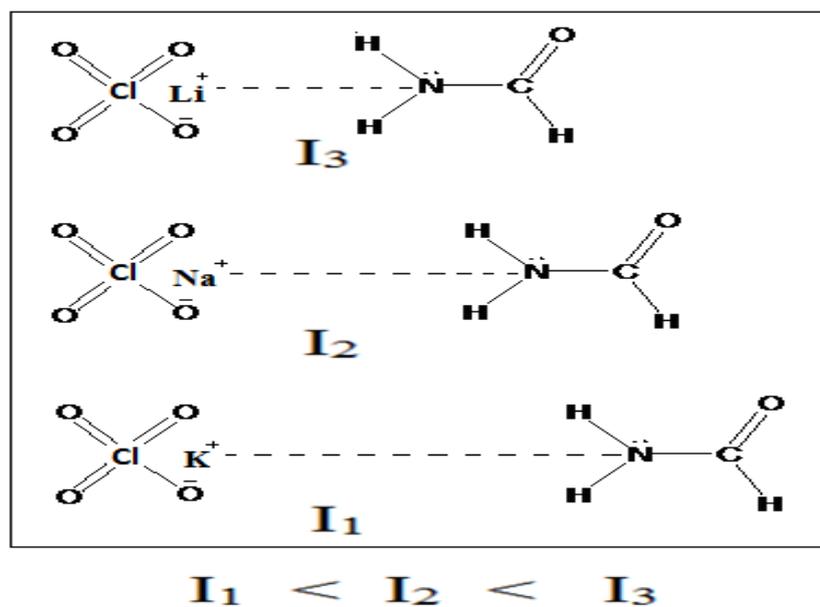
**Figure 1:** Apparent molar volume ( $\phi_v$ ), and the square root of concentrations ( $\sqrt{c}$ ) for LiClO<sub>4</sub> (—◆—), NaClO<sub>4</sub> (—■—) and KClO<sub>4</sub> (—▲—) in formamide at 298.15 K.



**Figure 2:** Plots of  $(\eta/\eta_0 - 1)/\sqrt{c}$  versus  $\sqrt{c}$  for LiClO<sub>4</sub> (—◆—), NaClO<sub>4</sub> (—■—) and KClO<sub>4</sub> (—▲—) in formamide at 298.15 K.



**Figure 3:** Apparent molar adiabatic compressibilities ( $\phi_K$ ) and the square root of concentrations ( $\sqrt{c}$ ) for LiClO<sub>4</sub> (—◆—), NaClO<sub>4</sub> (—■—) and KClO<sub>4</sub> (—▲—) in formamide at 298.15 K.



**Scheme 1.** Interaction of LiClO<sub>4</sub>, NaClO<sub>4</sub> and KClO<sub>4</sub> with Formamide .