

CHAPTER – V

PHYSICO-CHEMICAL STUDY OF SOLUTION BEHAVIOUR OF ALKALI METAL PERCHLORATES PREVAILING IN N, N- DIMETHYL FORMAMIDE WITH THE MANIFESTATION OF ION SOLVATION CONSEQUENCES

5.1. Introduction

Investigation on the transport properties of electrolytes has been utilized to understand the solvation and association behaviour of ions in different solvent media. Perchlorates are the high melting point inorganic salts easily soluble the protic solvents. Lithium Perchlorate is used in the manufacture of chemical sources of energy (i.e. fuel cells) for electric cars [1]. Sodium Perchlorate is extensively used to block iodine uptake for the patients with subclinical hyperthyroidism [2].

Measurement of Conductance has been employed to find out association and solvation behaviour of ions in solution. 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. Studies of apparent and limiting apparent molar volumes along with the viscosity have been used to elucidate the 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 N,N-Dimethyl Formamide at 298.15 K.

5.2. Experimental Methods

5.2.1. Materials

LiClO_4 , NaClO_4 and KClO_4 of puriss grade were obtained from Aldrich, Germany and used as purchased. N,N-Dimethyl Formamide of spectroscopy grade was procured from Sd. fine Chemicals and purified using standard methods [7].

5.2.2 Apparatus and Procedure

A stock solution for each of the metal perchlorates was prepared by mass 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 (ρ) was measured by a vibrating-tube Anton Paar density-meter (DMA 4500M) with a precision of 0.0005 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 Brookfield DV-III Ultra Programmable Rheometer with spindle size-42 having an accuracy of 1.0% and fitted to a Brookfield Digital Bath TC-500 at 298K using density and viscosity values from the literature [8-10]. The uncertainty in viscosity measurements is within $\pm 0.003 \text{ mPa s}$.

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 ± 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 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^{-1} . 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 $\pm 0.2 \text{ m.s}^{-1}$. The uncertainty for the working temperature was $\pm 0.02 \text{ K}$.

5.3. Results and Discussion

5.3.1. Conductance Calculation

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 (Λ) at various concentrations are reported in Table 2 and the conductance data for LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide have been investigated with the help of Fuoss conductance equation [15,16]. Three adjustable parameters limiting molar conductance (Λ_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.

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

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

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

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

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

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

where the relaxation field effect is denoted by R_x , E_L represents the electrophoretic counter current, k^{-1} denotes the radius of the ion atmosphere, e is the electron charge, ε 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, γ is the fraction of solute present as unpaired ion, α is the fraction of contact pairs, β is twice the Bjerrum distance, f is the activity coefficient and T is the absolute temperature. The computations were done with the help of programs suggested by Fuoss. Shedlovsky extrapolation of the data were employed to obtain the initial Λ_0 values for the iteration procedure. Input for the program is the set ($c_j, \Lambda_j, j=1, \dots, n$), n, ε, η, T , initial values of Λ_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 Λ_0 and α .

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

For a sequence of R values and then plotting δ against R , the minimum of the δ 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 detected in the δ - R curves for LiClO_4 , NaClO_4 and KClO_4 , in N,N-Dimethyl 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 denoted 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 ρ is its density. The values of Λ_0 , K_A , and R attained by this procedure are reported in Table 3.

Inspection of Table 3 shows that the limiting molar conductance Λ_0 is found to have an increasing order whilst moving from LiClO_4 , NaClO_4 followed by KClO_4 . The Table also reveals that the association in N,N-Dimethyl Formamide is highest for LiClO_4 and lowest for KClO_4 and intermediate in the case of NaClO_4 . Hence the ion-solvent interaction in N,N-Dimethyl Formamide is maximum in the case of LiClO_4 and minimum for KClO_4 . The ion-solvent interaction of NaClO_4 exists between LiClO_4 and KClO_4 . This leads to the fact that lowering of conductance of KClO_4 is found to be highest and lowest for LiClO_4 . The lowest viscosity of N,N-Dimethyl Formamide for KClO_4 also supports the above observation because with lowering of viscosity the Λ_0 value should increase [17].

The above trend in Λ_0 values can be supported through another characteristic function called the Walden product, $\Lambda_0 \eta$ given in Table 4. Even though the viscosity of N,N-Dimethyl Formamide for LiClO_4 is more than that of NaClO_4 and KClO_4 , the $\Lambda_0 \eta$ is found to attain an increasing order from LiClO_4 to KClO_4 which points out the predominance of Λ_0 over η .

ΔG° is given by the following relationship [18] and is given in Table 4.

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

The explanation of negative values of ΔG° can be made by considering the participation of specific covalent interaction in the ion-association process. The decrease in the value of ΔG° in N,N-Dimethyl Formamide for LiClO_4 than KClO_4

indicates the highest degree of association in LiClO_4 . K_A values are indicative of significant 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.

5.3.2. Density Calculation

The experimental value of densities of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide, as a function of concentration at 298.15K is listed in Table 5. limiting apparent molar volume is essential to investigate the interactions of LiClO_4 , NaClO_4 and KClO_4 in different concentrations of pure solvent. The apparent molar volumes ϕ_V given in Table 5 were found out 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, ρ and ρ_o are the densities of the solution and solvent, respectively. The limiting apparent molar volumes ϕ_V^0 were calculated in accordance with a least-squares treatment to the plots of ϕ_V versus \sqrt{c} using the following Masson equation [19]

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

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

The plots of ϕ_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 ϕ_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 ϕ_V^0 values. A perusal of Table 5 indicates that the ϕ_V^0 values are positive and is highest in case of LiClO_4 in N,N-Dimethyl Formamide. This indicates that maximum ion-solvent interaction in N,N-Dimethyl Formamide is found in the case of LiClO_4 and the same is minimum for KClO_4 . The said interaction of NaClO_4 becomes in between LiClO_4 and KClO_4 shown in the **Scheme 1** where **I₁**, **I₂** and **I₃**

are the extent of ion-solvent interaction of KClO_4 , NaClO_4 and LiClO_4 in N,N-Dimethyl Formamide respectively. The highest charge density and smallest size of Li^+ ion than that of Na^+ and K^+ favours the accessibility towards N,N-Dimethyl Formamide rendering to the highest ion solvent interaction which is enhanced by the following scheme and order. So the interaction of N,N-Dimethyl Formamide with Li^+ ion is maximum for LiClO_4 and minimum in the case of K^+ in KClO_4 .

On the other hand, 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 decrease in ion-ion interactions with the increase in dilution can be attributed to the increase in distance between ions at infinite dilution. The values of S_V^* indicate that the extent of ion-ion interaction in N,N-Dimethyl Formamide is highest for KClO_4 and lowest for LiClO_4 . From the comparison of the magnitude of ϕ_V^0 values with that of S_V^* , the former is found to be far greater than the latter in the solutions. This implies that ion-solvent interactions predominate over ion-ion interactions in all the solutions. Furthermore, the values of ϕ_V^0 lead to the fact that the lowest ion-solvent interaction of KClO_4 results in higher conductance than that of NaClO_4 whereas NaClO_4 exhibits higher conductance than LiClO_4 in N,N-Dimethyl Formamide.

5.3.3.. Viscosity Calculation

The viscosity data has been examined using Jones-Dole equation [20]

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

where η and η_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 that the A coefficients are smaller than the viscosity B -coefficients for all the solutions under investigation. This points towards weak ion-ion interactions in the solution. The viscosity B coefficient [21] describes the effects of ion-solvent interactions. Positive values of the viscosity B

coefficients for LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide reflects the presence of strong ion-solvent interactions. The viscosity B -coefficient value is found to be lowest for KClO_4 supporting the fact that the conductance is highest KClO_4 .

5.3.4. Ultrasonic Speed Calculation

The adiabatic compressibility (β_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 ρ is the density of solution. The apparent molar adiabatic compressibility (ϕ_K) of the solutions was found out from the relation,

$$\phi_K = M \beta_s / \rho + \int 1000(\beta_s \rho_o - \beta_o \rho) / c \rho \rho_o \quad (16)$$

Where β_s, β_o are the adiabatic compressibilities of the solution and solvent respectively and c is the molarity of the solution. Limiting apparent molar adiabatic compressibilities (ϕ_K^0) and experimental slopes (S_K^*) were achieved by fitting ϕ_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 β_s and ϕ_K are recorded in Table 7. Since the values of ϕ_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 ϕ_V^0 and S_V^* discussed earlier.

5.4. Conclusion

Extensive investigation of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide reveals that 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 KClO_4 in N,N-Dimethyl Formamide. The said interaction of NaClO_4 arises in the intermediacy of LiClO_4 and 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.

References

1. M. Jotanovic, Z. Andric, G. Tadric, V. Micic, *Peer-Reviewed and Open Access Journal* **2010**, 3, 15.
2. Becker C. *Radiologie* **2007**, 47(9), 768.
3. F.J. Millero, in: R.A. Horne (Ed.), *Structure Transport Process in Water Aqueous Solutions*, Wiley, New York, **1972**.
4. M.N. Roy, B. Sinha, V.K. Dakua, A. Sinha, *Pak. J. Sci. Ind. Res.* **2006**, 49, 153.
5. M.N. Roy, P. Pradhan, R.K. Das, P.G. Guha, *J. Chem. Eng. Data* **2008**, 53, 1417.
6. R. Chanda, M.N. Roy, *Fluid Phase Equilib.* **2008**, 269, 134.
7. D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd ed. Pergamon Press, Oxford, **1988**.
8. B. Sinha, V.K. Dakua, M.N. Roy, *J. Chem. Eng. Data.* 2007, 52, 1768.
9. J.A. Dean, *Lange's Handbook of Chemistry*, 11th ed. McGraw-Hill Book Company, New York, **1973**.
10. B.D. Chatterjee, *J. Chem. Eng. Data.* **2006**, 51, 1352.
11. J.E. Lind Jr., J.J. Zwolenik, R.M. Fuoss, *J. Am. Chem. Soc.* **1959**, 81, 1557.
12. M.N. Roy, A. Jha, R. Dey, *J. Chem. Eng. Data.* **2001**, 46, 1327.
13. M.N. Roy, D.K. Hazra, *Indian J. Chem. Technol.* **1994**, 1, 93.
14. R.M. Fuoss, *Proc. Natl. Acad. Sci. U.S.A.* **1978**, 75, 16.
15. R.M. Fuoss, *J. Phys. Chem.* **1978**, 82, 2427.
16. J. Barthel, M.B. Rogac, R. Neueder, *J. Solut. Chem.* **1999**, 28, 1071.
17. M.N. Roy, R. Dewan, D. Ekka, I. Banik, *Thermochimica Acta.* **2013**, 559, 46.
18. R.M. Fuoss and C.A. Kraus, *J. Am. Chem. Soc.* **1933**, 55, 2387.
19. F.J. Millero, A.L. Surdo, C. Shin, *Phys. Chem.* **1978**, 82, 784.
20. G. Jones, M. Dole, *J. Am. Chem. Soc.* **1929**, 51, 2950.

21. V. Minkin, O. Osipov, Y. Zhdanov, *Dipole Moments in Organic Chemistry*, Plenum Press, New York, London, **1970** .
22. M. I. Aralaguppi, C.V. Jadar, T.M. Aminabhavi, J.D. Ortego, S.C. Mehrotra, *J. Chem. Eng. Data* **1997**, *42* , 301.
23. V. A. Aminabhavi, T.M. Aminabhavi, R.H. Balundgi, *Ind. Eng. Chem. Res.* **1990**, *29*, 2106.

Table 1. Density (ρ), viscosity (η), refractive index (n_D) and dielectric constant (ϵ) of pure N,N Dimethyl Formamide at 298.15K.

Solvent	$\rho \times 10^{-3} (\text{kg m}^{-3})$		$\eta (\text{mPa s})$		$u (\text{ms}^{-1})$		ϵ
	Expt.	Lit.	Expt.	Lit.	Expt.	Lit.	
DMF	0.94484	0.9449	0.819	0.8209[23]	1449.7	1451.0[22]	36.7
		[22]					

Table 2. The concentration (c) and molar conductance (Λ) of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide at 298.15 K.

$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)	$c \times 10^4$ (mol.dm ⁻³)	$\Lambda \times 10^4$ (S. m ² .mol ⁻¹)
LiClO_4		NaClO_4		KClO_4	
1.1990	10.74	1.8796	12.99	4.8312	12.88
1.4232	10.61	2.6147	12.77	5.4850	12.76
1.7796	10.44	3.2580	12.58	6.3303	12.58
2.0136	10.33	3.8064	12.36	6.9960	12.41
2.2052	10.22	4.1943	12.23	7.3495	12.34
2.3994	10.13	4.9195	12.01	7.8456	12.18
2.6929	9.97	5.5178	11.86	8.3002	12.06
2.9447	9.84	6.3353	11.62	9.1144	11.96
3.1648	9.71	6.9960	11.46	9.7157	11.81
3.5081	9.56	7.4748	11.31	10.2913	11.69
3.6749	9.47	7.7785	11.19	11.1890	11.49
3.9521	9.34	8.0316	11.15	11.8818	11.39
4.2477	9.18	8.6260	10.91	12.3482	11.24
4.4437	9.09	9.4741	10.70	13.0393	11.14

Table 3. Limiting molar conductivity (Λ°), association constant (K_A), co-sphere diameter (R) and standard deviations (δ) of experimental Λ of LiClO_4 , NaClO_4 and KClO_4 at 298.15 K from eqn (3).

Salts	Solvent	$\Lambda^\circ \times 10^4$ ($\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$)	K_A ($\text{dm}^3\cdot\text{mol}^{-1}$)	R (\AA)	δ
LiClO_4	N,N-Dimethyl Formamide	11.945	929.379	8.6285	0.05131
NaClO_4		14.237	466.821	8.9585	0.07266
KClO_4		15.057	389.625	9.3185	0.04347

Table 4. Walden product ($\Lambda^\circ\eta_0$) and Gibb's energy change (ΔG°) of LiClO_4 , NaClO_4 and KClO_4 in N,N-Dimethyl Formamide at 298.15 K.

Solute	$\Lambda^\circ\eta_0$ ($\text{Sm}^2\text{mol}^{-1}$ mPass)	$\Delta G^\circ \times 10^{-4}$ (J mol^{-1})
LiClO_4	9.783	-1.6942
NaClO_4	11.659	-1.5235
KClO_4	12.332	-1.4786

Table 5. Experimental values of densities (ρ), apparent molar volume (ϕ_V), limiting apparent molar volume (ϕ_V^0) and experimental slope (S_V^*) of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol.dm ⁻³)	$\rho \times 10^{-3}$ (kg m ⁻³)	$\phi_V \times 10^6$ (m ³ ·mol ⁻¹)	$\phi_V^0 \times 10^6$ (m ³ ·mol ⁻¹)	$S_V^* \times 10^6$ (m ² ·mol ^{-3/2} L ^{1/2})
LiClO ₄ in N,N-Dimethyl Formamide				
0.0159	0.94516	90.02		
0.0318	0.94557	86.85		
0.0478	0.94605	84.14	98.42	-65.60
0.0638	0.94658	81.91		
0.0799	0.94716	79.86		
0.0959	0.94778	78.03		
NaClO ₄ in N,N-Dimethyl Formamide				
0.0157	0.94544	86.72		
0.0317	0.94614	83.54	94.42	-61.48
0.0476	0.9469	80.93		
0.0637	0.94771	78.88		
0.0796	0.94855	77.08		
0.0958	0.94944	75.43		
KClO ₄ in N,N-Dimethyl Formamide				
0.0160	0.94576	82.15		
0.0319	0.94677	78.71	89.93	-62.00
0.0479	0.94783	76.47		
0.0639	0.94895	74.27		
0.0799	0.95011	72.35		
0.0961	0.95131	70.74		

Table 6. Experimental values of concentration (c), viscosity (η), $(\eta/\eta_0 - 1)/c^{1/2}$, viscosity A,B- coefficients of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol dm ⁻³)	η (mPa s)	$(\eta/\eta_0 - 1)/c^{1/2}$ (Kg ^{1/2} mol ^{-1/2})	A (L mol ⁻¹)	B (L ^{1/2} mol ^{-1/2})
LiClO ₄ in N,N-Dimethyl Formamide				
0.0159	0.836	0.165		
0.0318	0.852	0.226		
0.0478	0.868	0.274	0.010	1.211
0.0638	0.884	0.314		
0.0799	0.901	0.354		
0.0959	0.917	0.386		
NaClO ₄ in N,N-Dimethyl Formamide				
0.0157	0.829	0.097		
0.0317	0.838	0.130		
0.0476	0.847	0.157	0.015	0.650
0.0637	0.856	0.179		
0.0796	0.865	0.199		
0.0958	0.874	0.217		
KClO ₄ in N,N-Dimethyl Formamide				
0.0160	0.826	0.068		
0.0319	0.831	0.082		
0.0479	0.836	0.095	0.025	0.320
0.0639	0.841	0.106		
0.0799	0.846	0.117		
0.0961	0.851	0.126		

Table 7. Experimental values of speed of sound (u), adiabatic compressibility (β_s) and apparent molar adiabatic compressibility (ϕ_K), limiting apparent molar adiabatic compressibility (ϕ_K^0), and experimental slopes (S_K^*) of LiClO₄, NaClO₄ and KClO₄ in N,N-Dimethyl Formamide at 298.15 K.

c (mol dm ⁻³)	u (m s ⁻¹)	$\beta_s \times 10^{10}$ (Pa ⁻¹)	$\phi_K \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)	$\phi_K^0 \times 10^{10}$ (m ³ mol ⁻¹ Pa ⁻¹)	$S_K^* \times 10^{10}$ (m ³ mol ^{-3/2} Pa ⁻¹ kg ^{1/2})
LiClO ₄ in N,N-Dimethyl Formamide					
0.0159	1453.5	5.0080	-1.413		
0.0318	1468.3	4.9054	-3.915		
0.0478	1491.6	4.7510	-5.910		
0.0638	1520.9	4.5671	-7.402	4.555	-47.50
0.0799	1559.6	4.3406	-8.870		
0.0959	1606.7	4.0872	-10.150		
NaClO ₄ in N,N-Dimethyl Formamide					
0.0157	1454.8	4.9976	-2.157		
0.0317	1471.3	4.8825	-4.717		
0.0476	1495.4	4.7226	-6.586		
0.0637	1526.8	4.5265	-8.109	3.619	-46.55
0.0796	1567.1	4.2929	-9.550		
0.0958	1615.3	4.0367	-10.736		
KClO ₄ in N,N-Dimethyl Formamide					
0.0160	1455.7	4.9897	-2.652		
0.0319	1472.9	4.8687	-5.169		
0.0479	1497.6	4.7041	-6.973		
0.0639	1530.8	4.4970	-8.594	3.061	-45.77
0.0799	1570.6	4.2667	-9.881		
0.0961	1619.5	4.0079	-11.039		

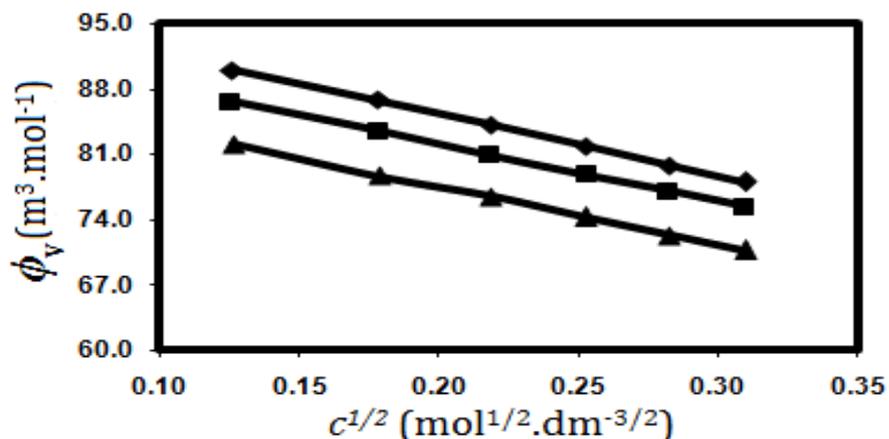


Figure 1: Apparent molar volume (ϕ_V) and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.

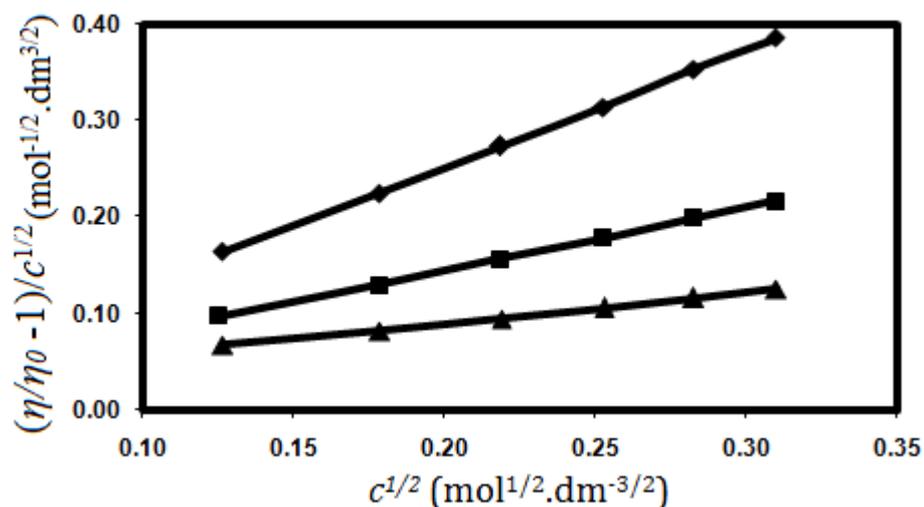


Figure 2: Plots of $(\eta/\eta_0 - 1)/\sqrt{c}$ versus \sqrt{c} for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.

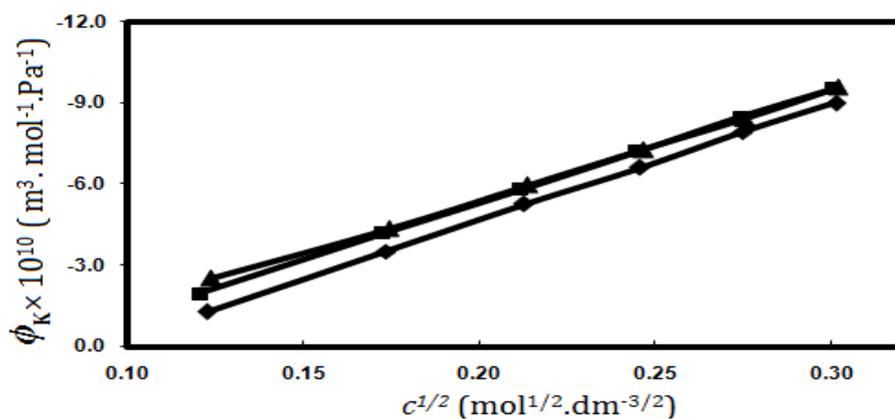
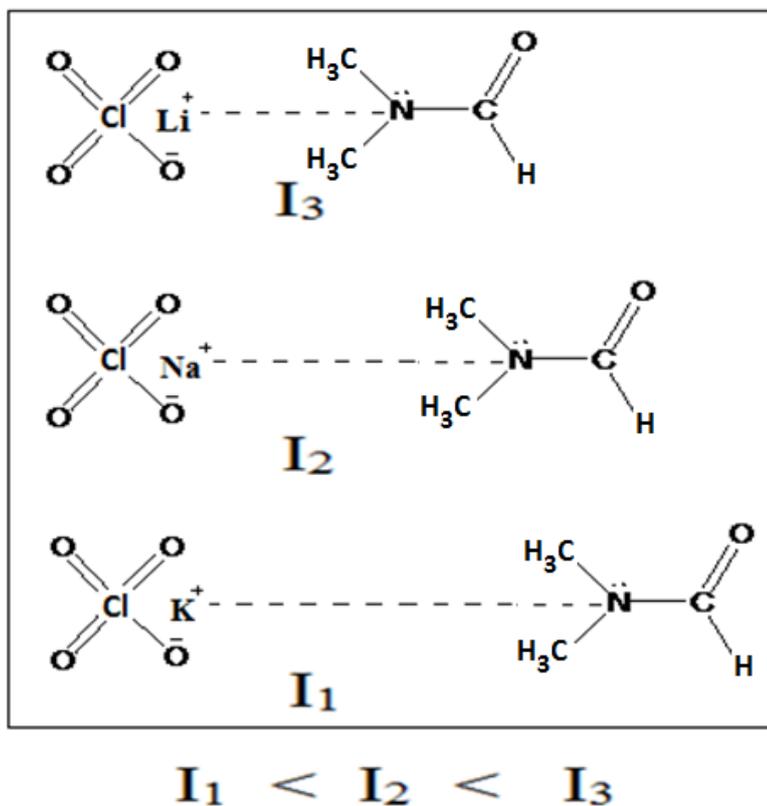


Figure 3: Apparent molar adiabatic compressibilities (ϕ_K) and the square root of concentrations (\sqrt{c}) for LiClO₄ (—◆—), NaClO₄ (—■—) and KClO₄ (—▲—) in N,N-Dimethyl Formamide at 298.15 K.



Scheme 1. Interaction of LiClO₄, NaClO₄ and KClO₄ with N,N-Dimethyl Formamide .