International Journal of Research in Advent Technology, Vol.7, No.4, April 2019
E-ISSN: 2321-9637
Available online at www.ijrat.org

Physicochemical Properties of $KClO_3$ in Aqueous NH_4NO_3 at Different Temperatures.

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Abstract: The study of the volumetric behaviour of $KClO_3$ as electrolytes in solution provides information useful to elucidate ion–ion, ion–solvent, and solvent–solvent interactions. Apparent molar volumes ($\emptyset_V$) and viscosity B-coefficients for $KClO_3$ solutions in aqueous 0.1% NH_4NO_3 and pure water system have been determined from density (ρ) and viscosity (η) measurements at 298.15 to 313.15 K using a pycnometer and Ubbelohde viscometer respectively. Masson's equation, Jones-Dole equation are used to study various interactions among the ion–ion, ion–solvent, and solvent–solvent. Further diffusion controlled reaction rate constant (k_d) are evaluated.
Keywords: $KClO_3$, density, viscosity, B-coefficient.

1. INTRODUCTION:

The design and operation of industrial processes that involve electrolyte solutions require knowledge of rigorous models or experimental data to represent the non ideality of the mixtures. Accurate predictions of densities and viscosities of mixed electrolyte solutions are of great importance in industry.[1] New measurements have continued to be made, focusing for example on the components of seawater and brines[2 - 4] or on extreme conditions such as very low or very high temperature.[5-11] Studies on viscosities, densities, and apparent molar volumes of ionic solutions assist in characterizing the structure and properties of solutions. Various types of interactions exist between the ions in solutions, and of these, ion-ion and ion-solvent interactions are of current interest in all branches of chemistry. The present investigation has been undertaken to enrich the data and provide better understanding of the nature of $KClO_3$ in presence 0.1% NH_4Cl and water.

Because of its activity against pathogens like salmonella and E.Coli., KClO3 is used as safe animal husbandry tool12 for economically important food animals like sheep ,cattle swine and poultry animals. Potassium chlorate is also measured in dietary supplements and flavour enhancing ingredients 13 and also in bottled drinking water or mineral water14. KClO3 analysis by chromatography, X-Rays and mass-spectrometry 15 were done and studied its contamination in food and water, but very fewer studies are done on its volumetric and viscometric properties. The importance of oxidizing agents towards the medical science leads us to undertake the present study.

2. EXPERIMENTAL:

***Materials*:**

$KClO_3$ of high purity was obtained from Research Lab Fine Chemicals, Mumbai, re-crystallized and then used. Deionized water with a specific conductance of < 10^{-6} $S.cm^{-1}$ was used for the preparation of solutions at room temperature in a molarity range (6.0×10^{-3} to 1.99×10^{-2}) $mol.L^{-1}$. The precision of balance used was ± 1×10^{-5}g.

Density Measurements:

The pycnometer was calibrated by measuring the densities of triple distilled water. The densities of $KClO_3$ solutions in aqueous 0.1% NH_4NO_3 and pure water were measured by bi-capillary pycnometer at different temperatures. The density was measured with an uncertainty of ±1.48 $\times10^{-4}$ $g.cm^{-3}$.

Viscosity Measurements:

The different compositions (0.0065M to 0.0365M) of solutions of $KClO_3$ were prepared in aqueous 0.1% NH_4NO_3 and pure water solvent systems. The viscosities were measured at 298.15, 303.15, 308.15, and 313.15K temperatures for seven different concentrations. The solution viscosities were measured with an uncertainty of ± 2.4×10^{-4} mPa.s by using Ubbelohde viscometer. The temperature of thermostat is maintained to desired temperature, by using demerstat with an accuracy of ± 0.1 K. The flow time will be measured at the accuracy of ± 0.01 s.

3. DATA EVALUATION:

The apparent molar volumes $\emptyset_V$, were obtained from the density results using the following equation [16-19]

$$\emptyset_V = \frac{1000(\rho_0-\rho)}{C\rho_0} + \frac{M2}{\rho} \qquad (1)$$

where M_2, C, ρ and ρ_0 are the molar mass of the $KClO_3$, concentration ($mol.L^{-1}$), and the densities of the solution and the solvent, respectively.

The apparent molar volumes ($\emptyset_V$) were plotted against the square root of concentration ($C^{½}$) in accordance with the Masson's equation[20].

$$\emptyset_V = \emptyset_V^0 + S_v.C^{½} \quad (2)$$

Where is the limiting apparent molar volume $\emptyset_V^0$ and S_v a semi-empirical parameter which depends on the nature of solute, solvent as well as temperature. The viscosity results for the aqueous solutions of $KClO_3$ in aqueous 0.1% NH_4NO_3 and pure water solvent systems were plotted in accordance with Jones-Dole equation[21]

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc \quad (3)$$

Where η_r = (η/η_o) and η, η_o are viscosities of the solution and solvent respectively, C is the molar concentration. The B-coefficients were obtained from the linear plots using the least-square fitting method. The A- coefficient reflects solute-solute interaction[22] and the B-coefficient reflect the solute-solvent interactions. Since in general, A/B <<1, the Jones – Dole equation reduces to,

$$\eta_r = l + \beta.C, \quad (4)$$

The relative viscosity data of these solutions have also been fitted in Moulik equation,

$$\eta_r^{\,2} = M + K\,C^2 \quad (5)$$

The density data of these solutions have also been fitted in Root's equation,

$$(d - d_0) / C = R - SC^{½} \quad (6)$$

where R and S are constants.

The diffusion controlled reaction rate constant k_d can be evaluated by using the viscosity data as

$$k_d = \frac{8RT}{3\eta} \quad (7)$$

The evaluated values are used to predict whether the solvolysis is fast or slow process.

4. RESULTS AND DISCUSSION:

The values of the densities (ρ) and viscosities (η) of $KClO_3$ in 0.1% NH_4NO_3 solvent systems and temperatures are reported Table-1. The table-1 reveals that densities and viscosities of KClO3 solutions under investigation decrease with increase in temperature and increases with increase in concentration. Such observations were previously made by Comesana et al.[23], Lee et al.[24,25] and Nikumbh et al.[26] for other solutions.

Apparent Molar Volumes ($\emptyset_V$) and Relative Viscosities (η_r) of $KClO_3$ in 0.1% NH_4NO_3 solvent systems and temperatures are reported in table-2. The positive values of $\emptyset_V$ increase with increase in concentration of 0.1% NH_4NO_3 and pure water solvent systems. The relative viscosities are found to increase with concentrations.

The apparent molar volumes at infinite dilution ($\emptyset_V^0 = V_2^0$) and slopes S_V, calculated using Masson equation (2) are given in table-3. The $\emptyset_V^0$ values of $KClO_3$ under investigation in 0.1% NH_4NO_3 and in pure water solvent systems are large and positive suggests presence of strong solute-solvent interactions promotes structure making effect.[27] .It is clear that the values of $\emptyset_V$ ($cm^3.mol^{-1}$) are positive and more or less similar in water and in salt solutions at different temperatures. The slope S_v is negative for $KClO_3$ solution in 0.1 % NH_4NO_3 and in pure water. Since S_v is measure of solute-solute interactions[28, 29].These results indicate that there is presence of strong solute-solute interactions. S_v values do not change systematically with change in temperature, and hence it suggests that the solute-solute interactions are insensitive to change in temperature.

The Diffusion reaction rate constant (k_d) evaluated by equation 7 and are reported in table-4. These values reveals that the solvolysis of $KClO_3$ in aqueous electrolyte studied is diffusion controlled rather than activated controlled process.

5. CONCLUSIONS:

In the present report, physicochemical properties of $KClO_3$ solutions in water and 0.1%NH_4NO_3 solutions at different temperatures are systematically presented. It has been observed that there exist strong solute– solvent interactions in these systems. The values of $\emptyset_V^0$ are positive suggest presence of ion-solvent interactions. The positive values of Jones-Dole coefficient 'B' suggesting strongly hydrated solute indicating structure promoting tendency i.e. kosmotropes(structure makers).The Moulik, Roots and Jones-Dole reduced equation are verified for $KClO_3$ solutions in 0.1%NH_4NO_3 solvent systems. The solvolysis of $KClO_3$ in water and 0.1%NH_4NO_3 solutions at different temperatures is diffusion controlled process.

Table 1: **Densities and Viscosities of $KClO_3$ solution in 0.1%NH_4NO_3 and distilled water at different temperatures**.

Solvent System	Molar Conc. of $KClO_3$ (C) mol/dm^3	Temperatures				Temperatures			
		298.15K	**303.15K**	**308.15K**	**313.15K**	**298.15K**	**303.15K**	**308.15K**	**313.15K**
		Density, (ρ) / (g.cm^{-3})				**Viscosity,** (η) / (mPa.s)			
0.1% NH_4NO_3	0.0065	0.99946	0.99808	0.99642	0.99468	1.007	1.0107	1.0128	1.0124
	0.0105	1.00089	0.99945	0.99783	0.99615	1.0115	1.0164	1.0187	1.0213
	0.0155	1.00264	1.00119	0.9996	0.99798	1.0171	1.0236	1.026	1.0323
	0.0215	1.00477	1.00328	1.00173	1.00018	1.0238	1.0323	1.0348	1.0455
	0.0285	1.00732	1.00576	1.00425	1.00271	1.0316	1.0423	1.0451	1.0609
	0.0365	1.01005	1.00849	1.00708	1.00567	1.0405	1.0539	1.0568	1.0785
Distilled water	0.0065	0.99908	0.99764	0.99590	0.99432	0.8955	0.8128	0.7307	0.6578
	0.0105	1.00033	0.99880	0.99718	0.99563	0.8965	0.8159	0.7360	0.6609
	0.0155	1.00190	1.00029	0.99880	0.99731	0.8978	0.8197	0.7426	0.6649
	0.0215	1.00373	1.00213	1.00073	0.99929	0.8993	0.8243	0.7505	0.6695
	0.0285	1.00596	1.00420	1.00299	1.00170	0.9011	0.8297	0.7596	0.6751
	0.0365	1.00844	1.00677	1.00557	1.00436	0.9031	0.8359	0.7701	0.6814

Table 2: **Apparent molar volumes and Relative viscosities of $KClO_3$ solution in 0.1%NH_4NO_3 and distilled water at different temperatures.**

Solvent System	Molar Conc. of $KClO_3$ (C) mol/dm^3	Temperatures				Temperatures			
		298.15K	**303.15 K**	**308.15 K**	**313.15 K**	**298.15 K**	**303.15 K**	**308.15 K**	**313.15 K**
		Apparent molar volumes, ($\emptyset_V$) /cm^3.mol^{-1}				**Relative viscosities,** (η_r)			
0.1% NH_4NO_3	0.0065	0.99863	0.99769	0.99559	0.99396	1.0070	1.0107	1.0128	1.0124
	0.0105	0.99982	0.99882	0.99678	0.99523	1.0115	1.0164	1.0187	1.0213
	0.0155	1.00131	1.00022	0.99826	0.99682	1.0171	1.0236	1.0260	1.0323
	0.0215	1.00305	1.00188	1.00001	0.99869	1.0238	1.0323	1.0348	1.0455
	0.0285	1.00518	1.00386	1.00206	1.00095	1.0316	1.0423	1.0451	1.0609
	0.0365	1.00756	1.00589	1.00453	1.00349	1.0405	1.0539	1.0568	1.0785
Distilled Water	0.0065	122.42	122.53	122.8	122.97	1.0012	1.0039	1.0059	1.0087
	0.0105	122.26	122.34	122.63	122.8	1.0023	1.0077	1.0107	1.0160
	0.0155	122.06	122.18	122.44	122.59	1.0037	1.0124	1.0167	1.0251
	0.0215	121.85	121.98	122.22	122.36	1.0054	1.0181	1.0239	1.0360
	0.0285	121.58	121.74	121.96	122.08	1.0074	1.0248	1.0323	1.0486
	0.0365	121.29	121.5	121.66	121.76	1.0096	1.0324	1.0419	1.0631

Table 3: Masson($\emptyset_V^0$, S_v,) Moulik(M,K) Jone-Dole (A,B) and Roots(R,S) parameters of $KClO_3$ solution in 0.1%NH_4NO_3 and distilled water at different temperatures.

Parameters	Temp (K)	0.1% NH_4NO_3	Distilled water	Parameter	Temp K)	0.1% NH_4NO_3	Distilled Water
$\emptyset_V^0$	298.15	123.2	123.3	**A**	298.15	0.00	-0.01
	303.15	123.4	123.2		303.15	0.02	-0.04
	308.15	123.8	123.9		308.15	0.05	-0.05
	313.15	123.8	123.3		313.15	0.03	-0.03
S_v	298.15	-11.78	-10.21	B	298.15	1.13	0.32
	303.15	-11.70	-8.85		303.15	1.36	1.09
	308.15	-13.04	-10.92		308.15	1.26	2.01

	313.15	-12.20	-10.19		313.15	2.32	1.32
M	298.15	1.02	1.00	**R**	298.15	0.34	0.24
	303.15	1.03	1.01		303.15	0.33	0.26
	308.15	1.03	1.03		308.15	0.11	0.24
	313.15	1.03	1.02		313.15	0.33	0.26
K	298.15	51.37	12.61	S	298.15	0.08	0.29
	303.15	66.77	43.44		303.15	0.10	0.30
	308.15	68.18	84.38		308.15	0.08	0.27
	313.15	103.50	55.23		313.15	0.13	0.30

Table4: Diffusion reaction rate constant k_d ($L\ mol^{-1}\ s^{-1}$) values of $KClO_3$ solution in 0.1 % NH_4NO_3.

Solvent System	Molar Conc. of KClO3 (C) mol/dm^3	Temperatures			
		298.15K	**303.15K**	**308.15K**	**313.15K**
		Diffusion reaction rate constant k_d ($L\ mol^{-1}\ s^{-1}$) x 10^{10}			
0.1% NH_4NO_3	0.0065	7.33	8.18	9.19	10.47
	0.0105	7.30	8.13	9.13	10.38
	0.0155	7.26	8.07	9.07	10.27
	0.0215	7.21	8.00	8.99	10.14
	0.0285	7.16	7.93	8.90	9.99
	0.0365	7.09	7.84	8.80	9.83

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