Revealing the Toxicity of Chlorate Through the Analysis of Molecular Interaction using Viscosity Measurements and Apparent Molar Volumes

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http://dx.doi.org/10.13005/ojc/370610

(Received: October 20, 2021; Accepted: December 02, 2021)

ABSTRACT

While chlorate has the ability to induce flowering in longan, it also has adverse impacts on the crop. Revealing the toxicity of chlorate in the environment is more than just about the environment and about human health, as well. Because of the large introduction of this chemical into the environment from the paper processing industry, there is indeed a lot of concern about its toxicity. Chlorate toxicology in the longan plant has been thoroughly investigated in solutions using viscosities and apparent molar volumes. The hydration of molecules and volume changes are involved in various chemical and biological processes in plant tissues, and their complete understanding demands a good idea for volumetric and viscometric study. It offers good data acquisition techniques for solute, solvent and solvent-solvent interactions. Multi-component systems containing KClO3 + water + ionic solid (ionic solids = KCl, KNO3, NH4NO3 and KH2PO4, are currently being worked out to study the dependence of transport properties of potassium chlorate in aqueous electrolyte solutions, with concentrations and temperature of solutions. The assessed kd values are used to predict whether the solvolysis of KClO3 in the presence of other electrolytes is a quick or slow process.

Keywords: Toxicity, KClO3, Volumetric and Viscometric properties, Diffusion controlled Reaction Rate Constant k_d.

INTRODUCTION

Lychees and longans are close family members. longans and lychees are comparable in nutritional composition. Both are minimal in calories and carbohydrates and are nil in fat. The antioxidants and fibres are abundant in longan and lychee similarly are great source of vitamin C.

Fig. 1. Lychee Fruit
of fireworks and matching bands also involves extensively utilised potassium chlorate. In smoke compositions such as smoke grenades it is utilised as a component. In laboratories and educational facilities, potassium chlorate is used to generate oxygen, other than explosives. It is also utilised for the destruction of pests as a pesticide in agriculture. (https://www.businesswire.com/portal/site/home/my-business-wire/, 2020).

A significant amount of information is needed on the properties of transport, thermodynamic and solution to comprehend how the co-solvent or co-solute can change the nature and structure of the water. (Bahadur, 2019).

This work examines the interaction like ion-solvent, ion-ion and solvent-solvent of potassium chlorate with aqueous ionic salts, as both the solute and solvents are utilised for agricultural operations. In this study the chemical and the electrostatic effect due to dielectric constant of the co-solute which are already present in soil like KCl, KNO3 and NH4NO3, KH2PO4 would play vital role in influencing solute-solvent interaction. (Ganjare, 2020). Viscosity data can be used to determine the diffusion controlled reaction rate constant $k_d$.

The current study used multi-component systems containing an ionic solid, water, and KClO3 (ionic solids = KCl, KNO3, and NH4NO3, KH2PO4) to evaluate the relationship between the transport properties of KClO3 solutions in aqueous electrolyte solutions and solution concentrations and temperature.

The densities of aqueous solutions were measured using 15 cm$^3$ double arm pycnometer in a transparent glass walled water bath. (Kharat, 2007) Triple distilled water was used to calibrate the pycnometer. At desired temperatures, the densities of KClO3 solutions in aqueous 1% KCl, KNO3 and NH4NO3, KH2PO4, and pure water were determined using a bi-capillary pycnometer. An average of triplicate measurements was the final result and the density was calculated with an accuracy of $\pm 1.25 \times 10^{-4}$ g.cm$^{-3}$. The thermostat temperature is maintained at the appropriate temperatures using a demerstat with an accuracy of $\pm 0.1$ K.

Viscosities of all salt solutions of ten different concentrations in water were measured using Ubbelohde viscometer at temperatures of 298.15,
303.15, 308.15, and 313.15K. Measurements to monitor reproducibility of results have been repeated at least three times. The overall precision of viscosity measurements was ±2.0×10^{-4} mPa.s. At 0.01 second intervals the flow time is accurately recorded. All chemicals were taken from Sigma Aldrich, Germany, with more than 99% purity and was further desiccated over anhydrous CaCl₂ before use. (Nanda, Nanda, & Mohanty, 2012). The sample specification is given in Table 1a,b.

### Table 1(a): Specification of Chemicals

| Chemicals           | Source            | Mass fraction | Purity          | Purification Method                  | CAS No.  | Mol. Mass g.Mol⁻¹ | Chemical Formula |
|---------------------|-------------------|---------------|-----------------|--------------------------------------|----------|------------------|------------------|
| Potassium Chlorate  | Sigma Aldrich     | ≥99.0%        | ≥99.0%          | desiccated over anhydrous CaCl₂       | 4/9/3811 | 122.55           | KClO₃            |
| Potassium Nitrate   | Sigma Aldrich     | ACS reagent   | ≥99.0%          | Used as obtained                      | 7757-79-1| 101.1            | KNO₃             |
| Potassium Chloride  | Sigma Aldrich     | ≥99.0%        | ≥99.0%          | Used as obtained                      | 7447-40-7| 74.55            | KCl              |
| Ammonium Nitrate    | Sigma Aldrich     | ACS reagent, | ≥98%            | Used as obtained                      | 6484-52-2| 80.04            | NH₄NO₃           |
| Potassium phosphate | Sigma Aldrich     | ≥98.0%        | Used as obtained| Used as obtained                      | 7778-77-0| 136.1            | KH₂PO₄           |

It is known the properties like density, viscosity, etc., are influenced by the presence of oxygen atom in a molecule. The presence of such groups increases the hydrophilicity and electrostriction between water and solute particles. (Nanda, Nanda, & Dalai, 2021).

### Data Evaluation

The apparent molar volumes \( \bar{V} \) were obtained from the density results using the following equation (Cui, et al., 2020) (Langore, Nikumbh, Patil, & Gaikwad, 2019).

\[
\bar{V} = \frac{1000(\rho_0 - \rho)}{C \rho} + \frac{M}{\rho}
\]

Where \( M \) is the molar mass of the KClO₃ in g mol⁻¹, \( C \) is the concentration (mol.L⁻¹), \( \rho \) and \( \rho_0 \) and the densities of the solution and the solvent, respectively in g cm⁻³.

The apparent molar volumes \( \bar{V} \) were plotted against the square root of concentration \( C^{1/2} \) in accordance with the Masson's equation. Partial molar volumes at infinite dilution were obtained by least-squares fitting to the equation: (Caro, 2020).

\[
\bar{V} = \bar{V}^0 + S_v C^{1/2}
\]

Where \( \bar{V}^0 \) is the limiting apparent molar volume and \( S_v \), a semi-empirical parameter which depends on the nature of solute, solvent as well as temperature.

### Table 1(b): Densities and Apparent molar volumes of KClO₃ solution in 1% KNO₃ and distilled water at different temperatures

| Molar Conc. (C) mol/dm³ | KClO₃ in 1% KCl | KClO₃ in 1% NH₄NO₃ | KClO₃ in 1% KNO₃ | KClO₃ in 1% KH₂PO₄ | Apparent molar volumes, \( \bar{V} \) cm⁻³ mol⁻¹ |
|-------------------------|----------------|--------------------|------------------|--------------------|-----------------------------------------------|
| Density, (ρ) (g.cm⁻³)   |                |                    |                  |                    |                                               |
| 0.0055                  | 1.00376        | 1.00578            | 1.00766          | 1.01016            | 121.43                                       |
| 0.0085                  | 1.00462        | 1.00632            | 1.0085           | 1.01173            | 121.34                                       |
| 0.0125                  | 1.00565        | 1.00718            | 1.00954          | 1.01304            | 121.2                                         |
| 0.0175                  | 1.00666        | 1.00889            | 1.0111           | 1.01459            | 121.09                                       |
| 0.0225                  | 1.0079         | 1.01026            | 1.01246          | 1.01626            | 120.92                                       |
| 0.0305                  | 1.00945        | 1.01162            | 1.01395          | 1.01845            | 120.82                                       |
| 0.0385                  | 1.0111         | 1.0135             | 1.01623          | 1.02043            | 120.65                                       |
| 0.0475                  | 1.0129         | 1.0158             | 1.01825          | 1.02297            | 120.45                                       |
| 0.0555                  | 1.0144         | 1.0176             | 1.0201           | 1.02519            | 120.32                                       |
| 0.0655                  | 1.0164         | 1.0196             | 1.0229           | 1.0282             | 120.18                                       |
| 0.0755                  | 1.0188         | 1.0217             | 1.0255           | 1.0316             | 120.01                                       |
| 0.0855                  | 1.0212         | 1.0239             | 1.0283           | 1.0350             | 120.00                                       |
| 0.0955                  | 1.0238         | 1.0263             | 1.0315           | 1.0385             | 120.00                                       |
| 0.1055                  | 1.0264         | 1.0287             | 1.0345           | 1.0420             | 120.00                                       |
| 0.303.15K               |                |                    |                  |                    |                                               |
The apparent molar volumes of transfer at infinite dilutions \( \Delta \phi^{\circ}_{v}(tr) \) of KClO\(_3\) obtained from the relation.

\[
\Delta \phi^{\circ}_{v}(tr) = \phi^{\circ}_{v}(\text{KClO}_3 \text{ in solvent system}) - \phi^{\circ}_{v}(\text{KClO}_3 \text{ in water})
\]

The positive \( \Delta \phi^{\circ}_{v}(tr) \) studied in the present investigation suggest that the ion-ion and ion-hydrophilic group interactions are stronger than the ion hydrophobic interaction that results in an increase in volume.

The viscosity results for the aqueous solutions of KClO\(_3\) in aqueous solute systems and pure water solvent systems were plotted in accordance with Jones-Dole equation (Lomesh, Nathan, Bala, & Thakur, 2019).

\[
\eta_r-1/C^{0.5} = A + BC^{0.5}
\]  

Where \( \eta_r = (\eta/\eta_o) \) and \( \eta, \eta_o \) are viscosities of the solution and solvent respectively, \( C \) is the molar concentration.

Table 2: Viscosities and Relative Viscosities of KClO\(_3\) solution in 1% KNO\(_3\) and distilled water at different temperatures

| Molar Conc. (C) mol/dm\(^3\) | KClO\(_3\) in 1% KCl | KClO\(_3\) in 1% NH\(_4\)NO\(_3\) | KClO\(_3\) in 1% KNO\(_3\) | KClO\(_3\) in 1% NH\(_2\)NO\(_3\) | KClO\(_3\) in 1% KCl | KClO\(_3\) in 1% NH\(_4\)NO\(_3\) | KClO\(_3\) in 1% KNO\(_3\) | KClO\(_3\) in 1% NH\(_2\)NO\(_3\) |
|-----------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| 298.15K                     | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) | Viscosities (\(\eta\)) (N-m\(^{-1}\)s) |
| 0.0055                      | 0.9296              | 0.9324              | 0.9359              | 0.9439              | 1.0358              | 1.0224              | 1.025               | 1.0239              |
| 0.0085                      | 0.9349              | 0.9368              | 0.9411              | 0.9491              | 1.0418              | 1.0283              | 1.0307              | 1.0289              |
| 0.0125                      | 0.9417              | 0.9448              | 0.9476              | 0.9556              | 1.0494              | 1.0356              | 1.0378              | 1.0335              |
| 0.0175                      | 0.9497              | 0.9508              | 0.9554              | 0.9624              | 1.0583              | 1.0444              | 1.0463              | 1.0474              |
| 0.0235                      | 0.9562              | 0.9601              | 0.9645              | 0.9715              | 1.0688              | 1.0546              | 1.0563              | 1.0579              |
| 0.0305                      | 0.9659              | 0.9708              | 0.9749              | 0.9819              | 1.0880              | 1.0664              | 1.0696              | 1.0699              |
| 0.0385                      | 0.9767              | 0.9817              | 0.9865              | 0.9915              | 1.0965              | 1.0785              | 1.0823              | 1.0856              |
| 0.0475                      | 0.9878              | 0.9938              | 0.9985              | 1.0045              | 1.1106              | 1.0924              | 1.1012              | 1.0997              |
| 0.0555                      | 0.9979              | 1.0023              | 1.0069              | 1.0136              | 1.1224              | 1.1064              | 1.1165              | 1.1115              |
| 303.15K                     | 298.15K             | 0.0055              | 0.0055              | 0.0055              | 0.0055              | 0.0055              | 0.0055              | 0.0055              | 0.0055              | 0.0055              |

The viscosity results for the aqueous solutions of KClO\(_3\) in aqueous solute systems and pure water solvent systems were plotted in accordance with Jones-Dole equation (Lomesh, Nathan, Bala, & Thakur, 2019).
Rathi. Orient. J. Chem., Vol. 37(6), 1336-1343 (2021)

The B-coefficients were obtained from the linear plots using the least-square fitting method. The A-coefficient reflects solute-solute interaction (Pérez-Durán, 2019) 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 density data of these solutions have also been fitted in Root’s equation,

$$(d-d_0)/C = R - SC^{1/2} \quad (6)$$

where R and S are constants.

The diffusion controlled reaction rate constant $k_d$ can be evaluated by using the viscosity data as (Rathi & Nikumbh, 2019).

### Table 3: Different parameters of KClO$_3$ in water and 1% KCl, KNO$_3$, NH$_4$NO$_3$ and KH$_2$PO$_4$ solution

| Temp     | Massons Parameters | Jone-Dole’s Parameters | Moulik Parameters | Roots Parameter | $\beta$ Values | $\Delta$ |
|----------|--------------------|------------------------|-------------------|-----------------|----------------|---------|
|          | $\rho_v$ (tr) | $\rho_0$ | $V_0$ | $S_v$ | $A/ B/ K$ | $M$ | $R$ | $S$ | $\beta$ | $\Delta$ |
| 298.15K | 121.3 | -10.21 | -0.01 | 0.32 | 12.61 | 1 | 0.24 | 0.29 | 0.28 | 0 |
| 303.15K | 121.2 | -8.57 | -0.04 | 1.09 | 43.44 | 1.02 | 0.26 | 0.3 | 0.95 | 0 |
| 308.15K | 121.9 | -10.92 | -0.05 | 2.01 | 84.38 | 1.03 | 0.24 | 0.27 | 1.81 | 0 |
| 313.15K | 121.3 | -10.19 | -0.03 | 1.32 | 55.23 | 1.02 | 0.26 | 0 | 1.2 | 0 |
| 298.15K | 121.9 | -4.05 | 0.03 | 0.35 | 40.18 | 1.04 | 0.52 | -1.39 | 0.87 | 0.4 |
| 303.15K | 121.9 | -4.03 | 0.05 | 0.93 | 55.7 | 1.03 | 0.53 | -1.5 | 1.22 | 0.7 |
| 308.15K | 121.1 | -3.89 | -0.03 | 1.58 | 74.91 | 1.03 | 0.54 | -1.5 | 1.61 | 0.2 |
| 313.15K | 122.2 | -3.16 | 0.03 | 1.79 | 99.02 | 1.04 | 0.55 | -1.6 | 2.1 | 0.9 |
| 298.15K | 121.8 | -7.71 | 0 | 1.14 | 52.04 | 1.02 | 1.45 | -5.53 | 1.13 | 0.5 |
| 303.15K | 122.1 | -7.81 | 0.02 | 1.21 | 58.8 | 1.02 | 1.47 | -5.7 | 1.27 | 0.9 |
| 306.15K | 122.2 | -7.56 | 0.01 | 1.52 | 72.89 | 1.03 | 1.28 | -4.75 | 1.57 | 0.3 |
| 313.15K | 122.4 | -7.77 | 0.01 | 2.06 | 97.91 | 1.04 | 1.53 | -6.03 | 2.09 | 1.1 |
| 298.15K | 121.9 | -10.63 | -0.03 | 1.57 | 57.27 | 1.03 | 1.45 | -5.17 | 1.47 | 0.6 |
| 303.15K | 122.1 | -10.53 | 0.1 | 0.86 | 68.16 | 1.02 | 1.46 | -5.21 | 1.24 | 0.9 |
| 308.15K | 122.3 | -10.69 | 0.06 | 1.17 | 64 | 1.03 | 1.5 | -5.5 | 1.38 | 0.4 |
| 313.15K | 122.6 | -11.18 | -0.02 | 1.94 | 86.68 | 1.03 | 1.39 | -4.86 | 1.86 | 1.3 |
| 298.15K | 121.9 | -10.25 | 0.02 | 1.57 | 56.32 | 1.03 | 1.46 | -5.27 | 1.27 | 1.8 |
| 303.15K | 123.3 | -9.73 | 0.15 | 0.86 | 66.17 | 1.02 | 1.45 | -5.23 | 1.23 | 2.1 |
| 308.15K | 123.5 | -10.55 | 0.03 | 1.17 | 71.24 | 1.03 | 1.53 | -5.51 | 1.27 | 1.6 |
| 313.15K | 123.7 | -10.7 | 0.02 | 1.94 | 89.35 | 1.03 | 1.29 | -4.76 | 1.46 | 2.4 |
The evaluated values are used to predict whether the solvolysis is fast or slow process.

### Table 4: Diffusion reaction rate constant \( k_d \) (L mol\(^{-1}\) s\(^{-1}\)) values of KClO\(_3\) water and 1 % KCl, KNO\(_3\), NH\(_4\)NO\(_3\) and KH\(_2\)PO\(_4\) solution

| Molar Conc. mol/dm\(^3\) | KClO\(_3\) in Water | 1% KCl | 1% NH\(_4\)NO\(_3\) | 1% KNO\(_3\) | KClO\(_3\) in KH\(_2\)PO\(_4\) in Water | 1% KCl | 1% NH\(_4\)NO\(_3\) | 1% KNO\(_3\) | KClO\(_3\) in KH\(_2\)PO\(_4\) |
|---------------------------|--------------------|--------|---------------------|-----------|-------------------------------------|--------|---------------------|-----------|--------------------------------|
| 0.0055                    | 7.38               | 7.23   | 7.21                | 7.18      | 7.16                                | 9.35   | 9.12                | 9.05      | 8.97                           |
| 0.0085                    | 7.37               | 7.21   | 7.18                | 7.14      | 7.13                                | 9.28   | 9.06                | 9.01      | 8.92                           |
| 0.0125                    | 7.36               | 7.18   | 7.14                | 7.09      | 7.06                                | 9.2    | 8.99                | 8.93      | 8.86                           |
| 0.0175                    | 7.35               | 7.14   | 7.09                | 7.03      | 7.04                                | 9.1    | 8.91                | 8.85      | 8.79                           |
| 0.0225                    | 7.34               | 7.11   | 7.03                | 6.96      | 6.94                                | 8.99   | 8.81                | 8.75      | 8.71                           |
| 0.0305                    | 7.32               | 7.09   | 6.97                | 6.88      | 6.86                                | 8.87   | 8.7                 | 8.65      | 8.62                           |
| 0.0385                    | 7.31               | 7.06   | 6.83                | 6.74      | 6.73                                | 7.91   | 7.83                | 8.56      | 8.38                           |
| 0.0475                    | 7.3               | 7.04   | 6.76                | 6.56      | 6.56                                | 7.87   | 7.71                | 8.34      | 8.17                           |
| 0.0555                    | 7.29               | 7.01   | 6.45                | 6.43      | 6.3                                | 7.68   | 7.64                | 8.11      | 8.01                           |

#### RESULT AND DISCUSSION

The values of densities and viscosities of KClO\(_3\) solutions decrease with increase in temperature and increases with increase in concentration. The apparent molar volume values of \( \phi_V \) decrease with concentration while the relative viscosities are found to increase with concentrations. The \( \phi_V^0 \) values of KClO\(_3\) under investigation in all solvent systems are large and positive. The \( S_v \) is negative. These results indicate that there is presence of strong solute-solute interactions. (Shekaari, 2019) The Diffusion reaction rate constant \( k_d \) values are positive and decrease with increase in temperature as well as concentration. Positive \( k_d \) values reveals that the solvolysis of KClO\(_3\) in aqueous electrolyte studied is diffusion controlled rather than activated controlled process.

#### CONCLUSION

The increase in densities and viscosities with concentration may be due to strengthening of solute-solvent interactions. (Gupta, 2019). All the investigated parameters has been revealed that there exist strong solute–solvent interaction.
amino acids and sugars. Excessive use of chlorate as a bleaching agent toxifies the water (Lubbers, Chauhan, & Bianchine, 1981), soil and disturbs the environment's equilibrium. (Kanitz, 1996). Reducing the usage of chlorate, used in the production of colours, safety matches, and explosives for tanning and finishing leather, is important in order to conserve and save the environment.

ACKNOWLEDGEMENT

I would like to sincerely acknowledge the guidance and help provided by Dr. Arun B. Nikumbh for compilation of this research report.

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