Density and Molar Refraction of KIO_3 in aqueous solutions of KCl at different temperatures.

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Abstract: Densities and Refractive Indices of solutions of potassium iodate (KIO3) have been studied in water and 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (w/v) aqueous solution of KCl with temperature in the range T = 298.15˚K- 313.15˚K. The data obtained is utilized to determine Specific Refraction (R_D) and Molar Refraction (R_M) of solutions. The values of Refractive indices, Molar Refraction (R_M) and Molar Polarisability (α) constant are found to be decreased with decreasing concentration of solute in solvent and these results are also interpreted in terms of interaction in salt solution. It has been verified that Molar Refraction is additive and constitutive property.

Key Words: Refractive index, Molar Refraction and Molar Polarisability.

1. Introduction :

Relevant information on electronic polarizability of individual ions in solution can be collected from refractive index and molar refractivity data [1] .The molar refractivity is a measure of the polarisability of the molecule. The study of specific refractivity, molar refractivity and polarisability of salt solutions plays an indispensable role not only in chemical but also in engineering, medical agriculture, food, oil, beverage industries and biotechnical field. Refractive index is useful for qualitative analysis of substances which gives idea about geometry and structure of molecule. The best part with the estimation of refractive index is that it can be measured easily with a high degree of accuracy.

Like $KClO_3$ and $KBrO_3$;KIO_3 is also one of the strong oxidizing agents [2]. KIO_3 can cause fires if it comes in contact with combustible materials or reducing agents. It has been used as a food additive, to prevent iodine deficiency; sometimes table salt is iodated using potassium iodate in place of potassium iodide as iodide can get oxidized easily in wet condition and in presence of molecular oxygen to iodine. In baking process, like potassium bromate, potassium iodate is also sometimes used as a maturing agent. In some countries, potassium iodate is also an ingredient in milk powders and baby formula milk and used as a source for dietary iodine. KIO_3 get decomposed in presence of heat, shock, friction, combustible materials, reducing materials, aluminium, organic compounds, carbon, hydrogen peroxide and sulphides. Potassium iodate may be used to protect against the health risks caused by accumulation of radioactive iodine in the thyroid by administrating and saturating the body with a stable source of iodine in the form of KIO_3 prior to exposure [3]. It is also approved by the World Health Organization that for radiation protection, potassium iodate (KIO_3) is the best alternative to potassium iodide (KI), as KI has poor shelf life in humid and hot climates [4]. The dye of Methyl Orange (MO) in water can be decolorized effectively in the presence of KIO_3 under UV irradiation.[5]

Measurement of refractive index is an essential and significant work to study the thermodynamic and other physical properties such as specific refractivity, molar refractivity and polarisability of solutions which provide valuable information about the molecular structure of the components used in the solutions [6]. The molar refractivity reflects arrangements of the electron shells of ions in molecule and yields information about the electronic polarization of ions. Molar refraction and polarisability constant of aqueous solutions of $KBrO_3$ has been studied in different concentration of ionic salts in water [7-8]. Refractive index, density, molar refraction and polarizability constant of substituted 2-oxo2Hchromene-3-carbohydrazide derivatives in different binary mixture are done [9]. Comparative study of refractive index of aqueous mixture of zinc and lead acetate at different temperature and different concentration has been done successfully [10]

The present paper deals with the study of molar refraction and polarisability constant of KIO_3 in aqueous KCl at different temperatures.

2. Experimental :

Materials:

The chemicals (KCl and KIO_3) were of high purity (ACS reagent ≥ 99.0%) obtained from Sigma Aldrich, used directly without further purification. Potassium iodate and potassium chloride are commercially available in the form of white crystals. Water used for solution preparation was triply distilled with specific conductance of < 10^{-6}S .cm^{-1}. Aqueous solutions of KCl of different percentage were prepared by dissolving an appropriate amount by weight of KCl in appropriate volume of water (w/v). The different concentrations of KIO_3 in KCl were prepared by diluting the stock solution. All weighing were done on electronic Contech balance having accuracy (0.0001g).

Density measurements:

Density measurements were performed using bi-capillary pycnometer. The pycnometer was calibrated by measuring the densities of triple distilled water. The density was measured with an uncertainty of ± 1.48 × 10^{-4} g.cm^{-3}. The temperatures were measured with an uncertainty of ± 0.01˚K.

Refractive index measurements:

Refractive indices of different solutions were measured with the help of Abbe's refractometer. The refractive indices values are referred to a wavelength of 589.3 nm (Na, D-line). The temperature of prism box was maintained constant at required temperature by circulating water from thermostat. The refractometer was calibrated by glass test pieces of known refractive indices supplied with the instrument.

3. Data Evaluation

The densities of solutions were determined from the relation as

$$d = M/V \qquad \ldots 1$$

Where 'M' is mass of solution in grams and 'V' is the volume of solution filled in the bi-capillary pycnometer in cubic centimeters.
The Electronic polarization (E), Specific Refraction (R_D), Molar refraction of solution (R_M) and Polarisability constant (α) of salt solutions were determined by following formulae [11-16].

$$E = n^2 \qquad \ldots 2$$

$$R_D = \frac{n^2-1}{n^2+2}\frac{1}{d} \qquad \ldots 3$$

$$R_M = \frac{n^2-1}{n^2+2} \times \frac{\sum X_i M_i}{d} \qquad \ldots 4$$

$$R_M = \frac{4}{3}\pi N \alpha \qquad \ldots 5$$

$$C_M = \frac{n^2-1}{n+0.4} \times \frac{1}{d} \qquad \ldots 6$$

Where 'n' is refractive index of solutions, 'X_i' is the mole fractions of water, KCl and KIO_3; 'M_i' is the molecular weights of water, KCl and KIO_3; 'N' is Avogadro's number.

4. Results and Discussion:

The present investigation includes the measurement of density and refractive index of salts in water at different temperatures is given in Table No. 1 and 2. The values of densities and refractive indices of KCl and KIO_3 in water increases with increase in concentration at all temperatures under investigation. The values however decrease with increase in temperature. The increase in concentration means increase in molar mass of salt and hence density increases. The increase in refractive index with increase in concentration is due to decrease in angle of refraction or increase in angle of incidence. The decrease in density with increase in temperature is due to increase in molar volume of solvent. However the decrease in refractive index is due to the fact that the solute-solute and solute-solvent interactions weaken with increase in temperature.

Densities followed the order KIO_3 > KCl for the same concentration of the salt. This is due to relative salvation, corresponding resultant volumes of system and molar mass of these salts.

The densities of both the salt solutions increased with increase in concentration in a given solution, which is because of strengthening of solute-solvent interactions. The refractive index of various solutions shows a linear relationship [17] with concentrations of potassium salts and is tabulated in Table No. 3, 4, 5, 6 and 7.Temperature dependent quantity, specific refraction (R_D) that characterizes electronic polarizability of a substance, this increasing magnitude R_D indicates strong solute-solvent interactions [18]. The salts under investigation are ionic. The molar refractivity values for individual cations and anions are measure of their respective deformability. On the basis of the results of Fajan's and co-workers [19] it can be concluded that

(a) The refractivity of anions is lowered by neighboring cations. It is lowered more in the presence of stronger electric field of the cation (a smaller radius and a greater charge) and more polarizable anion.
(b) The refractivity of cations is increased by the neighboring anions. Anions are thus more consolidated by cations and the electron shell of the cation is less rigid due to the effect of anions.
(c) The combination of ions to form molecules or crystals is then accompanied by a net decrease in the refractivity Δ [R_M].
(d) When consolidating effect of the cation on the anion counterbalance the loosening effect of the anion on the cation and vice versa. The additivity of the ionic refractivities in aqueous solutions at infinite dilution has been confirmed by Fajan's [20]

Table-1: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KIO_3 in 0.1% KCl at different temperatures.

Conc. of KIO_3 in 0.1% KCl ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarisability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)	Eykman's Constant, C_M ($cm^3.g^{-1}$)
298.15°K							
0.0065	1.00169	1.3329	1.7766	0.2053	3.7027	0.1468	0.4474
0.0105	1.00279	1.3329	1.7767	0.2051	3.7021	0.1468	0.447
0.0155	1.00416	1.333	1.7769	0.2049	3.7013	0.1467	0.4465
0.0215	1.00582	1.3331	1.7772	0.2046	3.7004	0.1467	0.4458

303.15˚K							
0.0065	0.99991	1.3323	1.7751	0.2053	3.7038	0.1468	0.4475
0.0105	1.00111	1.3324	1.7753	0.2051	3.7027	0.1468	0.447
0.0155	1.00260	1.3325	1.7754	0.2049	3.7014	0.1467	0.4464
0.0215	1.00439	1.3325	1.7756	0.2045	3.6999	0.1467	0.4457
308.15˚K							
0.0065	0.99838	1.3316	1.7731	0.2052	3.7016	0.1468	0.4472
0.0105	0.99961	1.3316	1.7732	0.205	3.7004	0.1467	0.4467
0.0155	1.00116	1.3317	1.7734	0.2047	3.6988	0.1466	0.4461
0.0215	1.00303	1.3317	1.7735	0.2044	3.6969	0.1466	0.4453
313.15˚K							
0.0065	0.99638	1.331	1.7715	0.2053	3.7029	0.1468	0.4473
0.0105	0.99770	1.331	1.7716	0.2051	3.7014	0.1467	0.4468
0.0155	0.99934	1.3311	1.7718	0.2047	3.6995	0.1467	0.4461
0.0215	1.00132	1.3311	1.7719	0.2044	3.6972	0.1466	0.4453

Table-2: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KIO_3 in 0.2% KCl at different temperatures.

Conc. of KIO_3 in 0.2% KCl ($mol.dm^{-3}$)	**Density, 'd' ($g.cm^{-3}$)**	**Refractive index, (n)**	**Electronic polarization (E)**	**Specific Refraction (R_D), ($g^{-1}.cm^3$)**	**Molar Refraction (R_M), ($cm^3.mol^{-1}$)**	**Polarisability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)**	**Eykman's Constant, C_M ($cm^3.g^{-1}$)**
298.15˚K							
0.0065	1.00256	1.333	1.7768	0.2052	3.7027	0.1468	0.4471
0.0105	1.00377	1.333	1.777	0.2049	3.7021	0.1468	0.4467
0.0155	1.00528	1.3331	1.7772	0.2047	3.7013	0.1467	0.4461
0.0215	1.00708	1.3332	1.7774	0.2044	3.7004	0.1467	0.4454
303.15˚K							
0.0065	1.00082	1.3325	1.7756	0.2052	3.7038	0.1469	0.4473
0.0105	1.00207	1.3326	1.7757	0.205	3.7027	0.1468	0.4468
0.0155	1.00358	1.3326	1.7759	0.2048	3.7014	0.1468	0.4462
0.0215	1.00541	1.3327	1.7761	0.2044	3.6999	0.1467	0.4455
308.15˚K							
0.0065	0.99928	1.3317	1.7735	0.2051	3.7016	0.1468	0.447
0.0105	1.00057	1.3318	1.7737	0.2049	3.7004	0.1467	0.4465
0.0155	1.00214	1.3318	1.7738	0.2046	3.6988	0.1467	0.4459
0.0215	1.00405	1.3319	1.774	0.2043	3.6969	0.1466	0.4451
313.15˚K							
0.0065	0.99786	1.3312	1.772	0.2051	3.7029	0.1468	0.4469
0.0105	0.99919	1.3312	1.7721	0.2049	3.7014	0.1467	0.4463
0.0155	1.00083	1.3312	1.7722	0.2045	3.6995	0.1466	0.4457
0.0215	1.00287	1.3313	1.7724	0.2042	3.6972	0.1465	0.4449

Table-3: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KIO_3 in 0.3% KCl at different temperatures.

Conc. of KIO_3 in 0.3% KCl ($mol.dm^{-3}$)	**Density, 'd' ($g.cm^{-3}$)**	**Refractive index, (n)**	**Electronic polarization (E)**	**Specific Refraction (R_D), ($g^{-1}.cm^3$)**	**Molar Refraction (R_M), ($cm^3.mol^{-1}$)**	**Polarisability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)**	**Eykman's Constant, C_M ($cm^3.g^{-1}$)**
298.15˚K							
0.0065	1.00331	1.3332	1.7774	0.2051	3.7175	0.1474	0.4471
0.0105	1.00462	1.3332	1.7775	0.2049	3.721	0.1475	0.4465
0.0155	1.00625	1.3333	1.7777	0.2046	3.7254	0.1477	0.4459
0.0215	1.00817	1.3334	1.7779	0.2042	3.7305	0.1479	0.4452

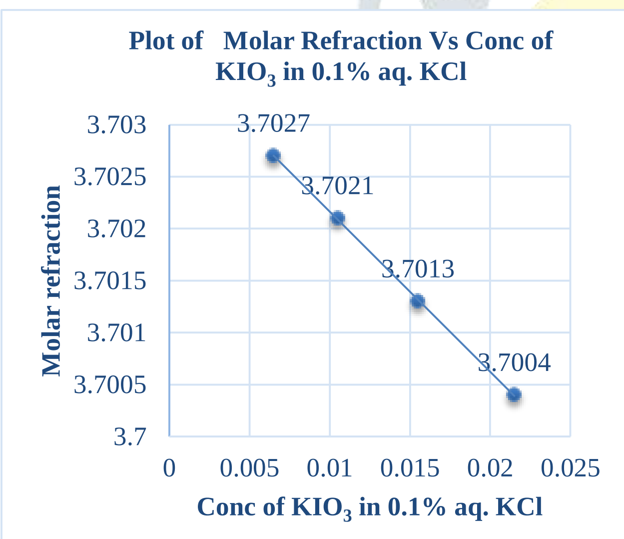
			303.15˚K				
0.0065	1.00215	1.3326	1.7758	0.205	3.7115	0.1471	0.4468
0.0105	1.00344	1.3326	1.7759	0.2048	3.715	0.1473	0.4463
0.0155	1.00505	1.3327	1.7761	0.2045	3.7193	0.1475	0.4457
0.0215	1.00698	1.3328	1.7763	0.2042	3.7244	0.1477	0.4449
			308.15˚K				
0.0065	1.00028	1.3319	1.7739	0.205	3.7041	0.1469	0.4467
0.0105	1.00161	1.3319	1.774	0.2048	3.7075	0.147	0.4462
0.0155	1.00327	1.332	1.7742	0.2045	3.7118	0.1472	0.4455
0.0215	1.00526	1.332	1.7743	0.2041	3.7168	0.1474	0.4447
			313.15˚K				
0.0065	0.99867	1.3313	1.7723	0.205	3.6982	0.1466	0.4467
0.0105	1.00004	1.3313	1.7725	0.2048	3.7017	0.1468	0.4461
0.0155	1.00172	1.3314	1.7726	0.2044	3.706	0.1469	0.4455
0.0215	1.00373	1.3315	1.7728	0.2041	3.7111	0.1471	0.4447

Table-4: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KIO_3 in 0.4% KCl at different temperatures.

Conc. of KIO_3 in 0.4% KCl ($mol.dm^{-3}$)	**Density, 'd' ($g.cm^{-3}$)**	**Refractive index, (n)**	**Electronic polarization (E)**	**Specific Refraction (R_D), ($g^{-1}.cm^3$)**	**Molar Refraction (R_M), ($cm^3.mol^{-1}$)**	**Polarisability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)**	**Eykman's Constant, C_M ($cm^3.g^{-1}$)**
			298.15˚K				
0.0065	1.00442	1.3333	1.7778	0.205	3.7056	0.1469	0.4468
0.0105	1.00583	1.3334	1.778	0.2047	3.7038	0.1468	0.4462
0.0155	1.00756	1.3335	1.7781	0.2044	3.7016	0.1468	0.4455
0.0215	1.00965	1.3335	1.7783	0.204	3.699	0.1467	0.4447
			303.15˚K				
0.0065	1.00298	1.3327	1.776	0.2049	3.7041	0.1469	0.4465
0.0105	1.00432	1.3327	1.7762	0.2047	3.7025	0.1468	0.446
0.0155	1.00603	1.3328	1.7763	0.2043	3.7006	0.1467	0.4453
0.0215	1.00809	1.3329	1.7766	0.204	3.6982	0.1466	0.4445
			308.15˚K				
0.0065	1.00154	1.332	1.7741	0.2048	3.7022	0.1468	0.4463
0.0105	1.00289	1.332	1.7743	0.2046	3.7006	0.1467	0.4457
0.0155	1.00458	1.3321	1.7744	0.2042	3.6986	0.1466	0.4451
0.0215	1.00659	1.3321	1.7746	0.2039	3.6962	0.1465	0.4443
			313.15˚K				
0.0065	1.00018	1.3315	1.7728	0.2048	3.7023	0.1468	0.4463
0.0105	1.00151	1.3315	1.7729	0.2046	3.7007	0.1467	0.4457
0.0155	1.00317	1.3316	1.7731	0.2042	3.6988	0.1466	0.4451
0.0215	1.00517	1.3316	1.7733	0.2039	3.6964	0.1465	0.4443

Table-5: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KIO_3 in 0.5% KCl at different temperatures.

Conc. of KIO_3 in 0.5% KCl ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarisability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)	Eykman's Constant, C_M ($cm^3.g^{-1}$)
298.15˚K							
0.0065	1.00518	1.3336	1.7784	0.2049	3.7076	0.147	0.4467
0.0105	1.00666	1.3336	1.7785	0.2047	3.7054	0.1469	0.4461
0.0155	1.00851	1.3336	1.7786	0.2043	3.7026	0.1468	0.4453
0.0215	1.01073	1.3337	1.7787	0.2039	3.6993	0.1467	0.4444
303.15˚K							
0.0065	1.00391	1.3328	1.7763	0.2048	3.7047	0.1469	0.4463
0.0105	1.00531	1.3328	1.7765	0.2045	3.7029	0.1468	0.4457
0.0155	1.00711	1.3329	1.7767	0.2042	3.7006	0.1467	0.445
0.0215	1.00925	1.333	1.7769	0.2038	3.6979	0.1466	0.4442
308.15˚K							
0.0065	1.00264	1.3322	1.7747	0.2047	3.7031	0.1468	0.4461
0.0105	1.00401	1.3322	1.7748	0.2044	3.7014	0.1467	0.4455
0.0155	1.00572	1.3323	1.775	0.2041	3.6993	0.1467	0.4448
0.0215	1.00775	1.3323	1.7751	0.2037	3.6967	0.1466	0.444
313.15˚K							
0.0065	1.00099	1.3316	1.7731	0.2047	3.703	0.1468	0.446
0.0105	1.00238	1.3316	1.7732	0.2044	3.7013	0.1467	0.4455
0.0155	1.00407	1.3317	1.7733	0.2041	3.6992	0.1467	0.4448
0.0215	1.00615	1.3317	1.7735	0.2037	3.6966	0.1466	0.444



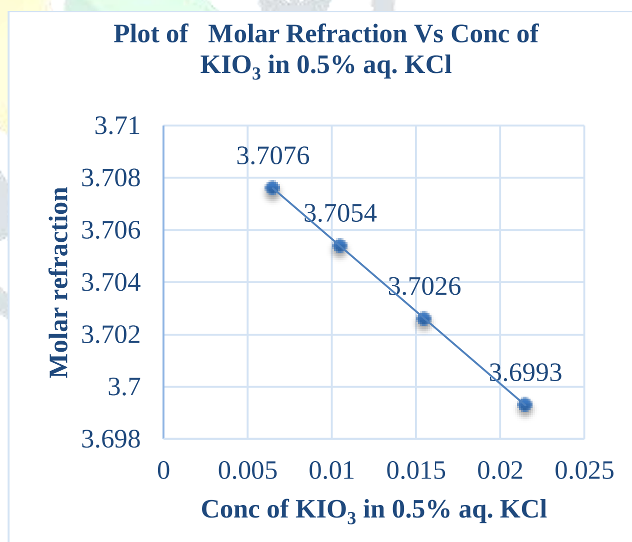


Table-6: Δ [R_M]values for Molar Refraction of KIO_3 in 0.5% KCl and Molar Refraction of KIO_3 in 0.1% KCl at different temperatures.

Concentration Of KIO_3 in water (mol.dm^{-3})	Temperature in °K	Δ R_M	Temperature in °K	Δ R_M	Temperature in °K	Δ R_M	Temperature in °K	Δ R_M
0.0065	**298.15**	0.0049	**303.15**	0.0009	**308.15**	0.0015	**313.15**	0.0009
0.0105		0.0033		0.0002		0.001		0.0004
0.0155		0.0013		0.0002		0.0005		0.0002
0.0215		0.0005		0.001		0.0006		0.0007

The analysis of present investigation shows that there is decrease in polarizability as well as molar refraction with increase in concentration of salts. C_M also decreases with increase in molar concentration of KIO_3 in 0.1-0.5 % KCl at all temperatures.[21] This may be due to dispersion force. It is the molecular force which arises from temporary dipole moment. The cumulative dipole-dipole interaction may create weak dispersion force resulting in increase in molar refraction and polarizability. Apart from the intrinsic usefulness of the *n* and *ρ* data, a structure-based comparison can help establish trends and identify possibly spurious results. [22] Table No. 8 shows positive values of Δ R_M. The molar refraction values of KIO3 in 0.5% KCl are higher than in KIO3 in 0.1 % KCl at all temperatures under investigation.

5. Conclusions:

From the data it can be concluded that

1. The higher values of densities of KIO_3 than KCl are due to the relative salvation, corresponding relative volumes of system and molar mass of the salts.
2. The increase in densities with concentration may be due to strengthening of solute-solvent interactions.
3. The increase in polarizability as well as molar refraction with increase in concentration of salts is due to dispersion force.
4. This increasing magnitude of R_D indicates strong solute-solvent interactions.
5. The molar refraction values of KIO3 in 0.5% KCl are higher than in KIO3 in 0.1% KCl, shows molar refraction is additive as well as constitutive property.
6. Rm values employed to explain interaction effects in electrolytic solutions. It can be calculated that interactions depend on the concentration and temperature. The polarizability of a compound is a measure of its molecular volume.

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