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RESEARCH ARTICLE

STUDY OF MOLAR REFRACTION AND POLARIZABILITY CONSTANT OF AQUEOUS SOLUTIONS OF KNO_3 AND $KBrO_3$ AT DIFFERENT TEMPERATURES.

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Abstract

Densities and Refractive Indices of solutions of potassium bromate ($KBrO_3$) have been studied in water and 0.1%, 0.2%, 0.3%, 0.4% and 0.5% (w/v) aqueous solution of KNO_3 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 Polarizability (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.

Introduction:-

The molar refractivity is a measure of the polarizability of the molecule [1]. The study of specific refractivity, molar refractivity and polarizability of salt solutions plays a vital role not only in chemical but also in engineering, medical and biotechnical field. The best part with measurement of refractive index is that it can be measured easily with a high degree of accuracy.

Potassium bromate has been widely used in the oxidation of many organic compounds in acidic medium. Idris S.O. et al.[2] describe the kinetics of the oxidation of L- Methionine by potassium bromate in hydrochloric acid medium. The kinetics and mechanism of the oxidation of Tartaric acid by potassium bromate in perchloric acidic medium was also studied[3]. A combination of sulfuric acid and potassium bromate in the presence of SiO_2 were used as effective oxidizing agent for the oxidation of alcohol to its corresponding aldehyde and ketone derivatives in various organic solvents with good yield[4].Potassium bromate as an oxidizing agent in a Titania-based Ru CMP slurry was studied by S. Noyel Victoria[5]. The toxic effect of $KBrO_3$ on vestibuloocular reflex system of human was studied[6]. Optical dispersion and Molar refractivities of Alkali Halide crystals and aqueous solutions were studied by A. Penzkofer, H. Glas[7]

Measurement of refractive index is an essential and important work to study the thermodynamic and other physical properties such as specific refractivity, molar refractivity and polarizability of solutions which provide information about the molecular structure of the components used in the solutions. The molar refractivity reflects arrangements of the electron shells of ions in molecule and yields information about the electronic polarization of ions.

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The present paper deals with the study of molar refraction and polarizability constant of $KBrO_3$ in aqueous KNO_3at different temperatures.

Experimental:-

Materials:-

The chemicals (KNO_3 and $KBrO_3$) were of high purity (ACS reagent ≥ 99.0%) obtained from Sigma Aldrich, used directly without further purification. Potassium bromate and potassium nitrate 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 KNO_3 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 $KBrO_3$ in KNO_3 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 $\pm 1.48 \times 10^{-4}$ 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.

Data Evaluation:-

The densities of solutions were determined from the relation as

$$d = M/V \quad (1)$$

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 Polarizability constant (α) of salt solutions were determined by following formulae [8-12].

$$E = n^2 \quad (2)$$

$$R_D = \frac{n^2-1}{n^2+2}\frac{1}{d} \quad (3)$$

$$R_M = \frac{n^2-1}{n^2+2} \times \frac{\sum X_i M_i}{d} \quad (4)$$

$$R_M = \frac{4}{3}\pi N \alpha \quad (5)$$

Where 'n' is refractive index of solutions, 'X_i' is the mole fractions of water, KNO_3 and $KBrO_3$; 'M_i' is the molecular weights of water, KNO_3 and $KBrO_3$; 'N' is Avogadro's number.

Results and Discussion:-

The present investigation includes the measurement of density and refractive index of KNO_3 and $KBrO_3$ in water at different temperatures is given in Table No. 1 and 2 respectively. The values of densities and refractive indices of KNO_3 and $KBrO_3$ 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.

The densities of both the salt solutions increase with increase in concentration, which is because of strengthening of solute-solvent interactions. The refractive index of various solutions shows a linear relationship[13] 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 [14]. The salts under investigation are ionic. The molar refractivity values for individual cations and anions are measure of their respective deformabilities. On the basis of the results of Fajan's and co-workers [15] it can be concluded that

1. 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.
2. 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.
3. The combination of ions to form molecules or crystals is then accompanied by a net decrease in the refractivity Δ [R_M]. When consolidating effect of the cation on the anion outweighs 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[16].

Table 1-: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of KNO_3 in water at different temperatures.

Conc.of aqueous KNO_3in percentage	**Density, 'd' ($g.cm^{-3}$)**	**Refractive index, (n)**	**Electronic polarization (E)**	**Specific Refraction (R_D), ($g^{-1}.cm^3$)**	**Molar Refraction (R_M), $cm^3.mol^{-1}$**	**Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)**
298.15˚K						
0.1	0.99818	1.3329	1.7766	0.2060	3.7120	0.1472
0.2	0.99948	1.3330	1.7769	0.2057	3.7131	0.1472
0.3	1.00083	1.3331	1.7772	0.2055	3.7146	0.1473
0.4	1.00216	1.3333	1.7777	0.2053	3.7165	0.1474
0.5	1.00350	1.3334	1.7779	0.2052	3.7173	0.1474
303.15˚K						
0.1	0.99572	1.3323	1.7750	0.2062	3.7077	0.1470
0.2	0.99673	1.3324	1.7753	0.2060	3.7014	0.1468
0.3	0.99746	1.3325	1.7756	0.2059	3.6960	0.1466
0.4	0.99826	1.3326	1.7758	0.2058	3.6905	0.1464
0.5	0.99931	1.3327	1.7761	0.2057	3.6841	0.1461
308.15˚K						
0.1	0.99417	1.3315	1.7729	0.2061	3.7054	0.1469
0.2	0.99518	1.3317	1.7734	0.2060	3.7000	0.1467
0.3	0.99592	1.3319	1.7740	0.2059	3.6957	0.1466
0.4	0.99672	1.3321	1.7745	0.2058	3.6912	0.1464
0.5	0.99755	1.3322	1.7748	0.2057	3.6856	0.1462
313.15˚K						
0.1	0.99250	1.3311	1.7718	0.2062	3.7075	0.1470
0.2	0.99350	1.3312	1.7721	0.2061	3.7012	0.1468
0.3	0.99438	1.3313	1.7724	0.2059	3.6954	0.1465
0.4	0.99518	1.3315	1.7729	0.2058	3.6908	0.1464
0.5	0.99617	1.3316	1.7732	0.2057	3.6846	0.1461

Table- 2:- Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in water at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15°K						
0.0035	0.99821	1.3325	1.7756	0.2059	3.7081	0.1471
0.0105	1.00033	1.3326	1.7759	0.2055	3.7048	0.1469
0.0215	1.00373	1.3327	1.7762	0.2049	3.6996	0.1467
0.0365	1.00844	1.3328	1.7769	0.2040	3.6917	0.1464
303.15°K						
0.0035	0.99672	1.3321	1.7746	0.2058	3.7075	0.1470
0.0105	0.99880	1.3322	1.7748	0.2054	3.7034	0.1468
0.0215	1.00213	1.3323	1.7751	0.2048	3.6980	0.1467
0.0365	1.00677	1.3324	1.7753	0.2039	3.6915	0.1464
308.15°K						
0.0035	0.99493	1.3313	1.7724	0.2057	3.7062	0.1470
0.0105	0.99719	1.3314	1.7726	0.2054	3.7025	0.1468
0.0215	1.00073	1.3315	1.7729	0.2047	3.6966	0.1466
0.0365	1.00557	1.3317	1.7734	0.2038	3.6889	0.1463
313.15°K						
0.0035	0.99338	1.3307	1.7708	0.2057	3.7060	0.1469
0.0105	0.99563	1.3308	1.7709	0.2053	3.7019	0.1468
0.0215	0.99929	1.3309	1.7713	0.2046	3.6955	0.1465
0.0365	1.00436	1.3311	1.7718	0.2037	3.6873	0.1462

Table 3:- Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in 0.1% KNO_3 at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15°K						
0.0035	1.00026	1.3330	1.7770	0.2057	3.7067	0.1470
0.0105	1.00290	1.3331	1.7772	0.2052	3.7020	0.1468
0.0215	1.00705	1.3333	1.7777	0.2045	3.6958	0.1466
0.0365	1.01268	1.3335	1.7782	0.2040	3.6940	0.1465
303.15°K						
0.0035	0.99943	1.3324	1.7754	0.2055	3.7039	0.1469
0.0105	1.00165	1.3325	1.7756	0.2051	3.7003	0.1467
0.0215	1.00517	1.3326	1.7759	0.2044	3.6946	0.1465
0.0365	1.00989	1.3328	1.7764	0.2036	3.6887	0.1463
308.15°K						
0.0035	0.99853	1.3316	1.7732	0.2052	3.6991	0.1467
0.0105	1.00041	1.3317	1.7735	0.2049	3.6971	0.1466
0.0215	1.00336	1.3318	1.7738	0.2044	3.6944	0.1465
0.0365	1.00727	1.3320	1.7742	0.2035	3.6871	0.1462
313.15°K						
0.0035	0.99769	1.3312	1.7721	0.2052	3.6980	0.1467
0.0105	0.99918	1.3313	1.7724	0.2049	3.6968	0.1466
0.0215	1.00153	1.3314	1.7727	0.2044	3.6932	0.1464
0.0365	1.00460	1.3316	1.7732	0.2034	3.6844	0.1462

Table 4:- Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in 0.2% KNO_3 at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15°K						
0.0035	1.00172	1.3331	1.7772	0.2054	3.7055	0.1469
0.0105	1.00475	1.3332	1.7775	0.2049	3.6992	0.1467
0.0215	1.00953	1.3334	1.7779	0.2040	3.6891	0.1463
0.0365	1.01599	1.3336	1.7785	0.2028	3.6760	0.1458
303.15°K						
0.0035	1.00078	1.3325	1.7756	0.2053	3.7027	0.1468
0.0105	1.00332	1.3326	1.7758	0.2048	3.6980	0.1467
0.0215	1.00742	1.3327	1.7762	0.2040	3.6905	0.1464
0.0365	1.01289	1.3329	1.7766	0.2030	3.6803	0.1459
308.15°K						
0.0035	1.00011	1.3318	1.7738	0.2050	3.6982	0.1467
0.0105	1.00219	1.3319	1.7740	0.2046	3.6953	0.1465
0.0215	1.00555	1.3321	1.7744	0.2040	3.6906	0.1464
0.0365	1.00998	1.3323	1.7750	0.2033	3.6848	0.1461
313.15°K						
0.0035	0.99948	1.3313	1.7724	0.2049	3.6955	0.1466
0.0105	1.00111	1.3314	1.7727	0.2046	3.6944	0.1465
0.0215	1.00369	1.3316	1.7731	0.2042	3.6926	0.1464
0.0365	1.00700	1.3318	1.7737	0.2036	3.6907	0.1464

Table-5: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in 0.3% KNO_3 at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15°K						
0.0035	1.00310	1.3332	1.7775	0.2052	3.7159	0.1474
0.0105	1.00648	1.3334	1.7778	0.2046	3.7210	0.1476
0.0215	1.01169	1.3335	1.7782	0.2036	3.7285	0.1479
0.0365	1.01894	1.3337	1.7788	0.2023	3.7389	0.1483
303.15°K						
0.0035	1.00220	1.3326	1.7759	0.2050	3.7099	0.1471
0.0105	1.00501	1.3327	1.7762	0.2045	3.7149	0.1473
0.0215	1.00945	1.3329	1.7767	0.2037	3.7226	0.1476
0.0365	1.01567	1.3331	1.7772	0.2026	3.7328	0.1480
308.15°K						
0.0035	1.00169	1.3320	1.7743	0.2048	3.7037	0.1469
0.0105	1.00392	1.3321	1.7746	0.2044	3.7086	0.1471
0.0215	1.00737	1.3323	1.7750	0.2038	3.7161	0.1474
0.0365	1.01216	1.3325	1.7756	0.2029	3.7267	0.1478
313.15°K						
0.0035	1.00126	1.3314	1.7727	0.2046	3.6978	0.1466
0.0105	1.00285	1.3315	1.7730	0.2043	3.7025	0.1468
0.0215	1.00541	1.3317	1.7734	0.2039	3.7101	0.1471
0.0365	1.00877	1.3319	1.7740	0.2033	3.7206	0.1475

Table-6: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in 0.4% KNO_3 at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15˚K						
0.0035	1.00479	1.3334	1.7780	0.2050	3.7033	0.1469
0.0105	1.00843	1.3335	1.7783	0.2043	3.6947	0.1465
0.0215	1.01418	1.3337	1.7787	0.2036	3.6888	0.1463
0.0365	1.02212	1.3339	1.7793	0.2030	3.6855	0.1462
303.15˚K						
0.0035	1.00401	1.3327	1.7762	0.2047	3.6991	0.1467
0.0105	1.00698	1.3328	1.7765	0.2042	3.6930	0.1465
0.0215	1.01168	1.3330	1.7769	0.2035	3.6865	0.1462
0.0365	1.01818	1.3332	1.7774	0.2025	3.6829	0.1461
308.15˚K						
0.0035	1.00331	1.3322	1.7748	0.2046	3.6966	0.1466
0.0105	1.00565	1.3323	1.7751	0.2042	3.6927	0.1464
0.0215	1.00932	1.3324	1.7754	0.2034	3.6835	0.1461
0.0365	1.01446	1.3326	1.7758	0.2021	3.6775	0.1459
313.15˚K						
0.0035	1.00282	1.3316	1.7733	0.2044	3.6924	0.1464
0.0105	1.00449	1.3317	1.7735	0.2041	3.6910	0.1464
0.0215	1.00709	1.3318	1.7738	0.2033	3.6812	0.1460
0.0365	1.01062	1.3320	1.7742	0.2017	3.6770	0.1458

Table 7:- Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarizability constant (α) of $KBrO_3$ in 0.5% KNO_3at different temperatures.

Conc.of $KBrO_3$in water ($mol.dm^{-3}$)	Density, 'd' ($g.cm^{-3}$)	Refractive index, (n)	Electronic polarization (E)	Specific Refraction (R_D), ($g^{-1}.cm^3$)	Molar Refraction (R_M), ($cm^3.mol^{-1}$)	Polarizability constant (α) × 10^{-23} ($cm^3.mol^{-1}$)
298.15˚K						
0.0035	1.00626	1.3336	1.7784	0.2047	3.7021	0.1468
0.0105	1.01024	1.3337	1.7787	0.2040	3.6924	0.1464
0.0215	1.01648	1.3338	1.7790	0.2028	3.6840	0.1463
0.0365	1.02520	1.3340	1.7796	0.2012	3.6792	0.1459
303.15˚K						
0.0035	1.00600	1.3328	1.7765	0.2044	3.6959	0.1466
0.0105	1.00940	1.3329	1.7767	0.2037	3.6895	0.1463
0.0215	1.01483	1.3331	1.7771	0.2027	3.6825	0.1462
0.0365	1.02213	1.3333	1.7777	0.2014	3.6727	0.1456
308.15˚K						
0.0035	1.00513	1.3323	1.7751	0.2043	3.6939	0.1465
0.0105	1.00763	1.3324	1.7753	0.2038	3.6882	0.1463
0.0215	1.01153	1.3325	1.7757	0.2031	3.6771	0.1461
0.0365	1.01690	1.3327	1.7761	0.2021	3.6599	0.1454
313.15˚K						
0.0035	1.00465	1.3317	1.7735	0.2040	3.6896	0.1463
0.0105	1.00651	1.3318	1.7737	0.2037	3.6875	0.1462
0.0215	1.00943	1.3319	1.7741	0.2032	3.6760	0.1460
0.0365	1.01344	1.3321	1.7745	0.2025	3.6559	0.1453

Table 8:- Δ [$R_{M]}$ values for Molar Refraction of $KBrO_3$in 0.5% KNO_3 and Molar Refraction of $KBrO_3$in water at different temperatures.

Concentration of $KBrO_3$ in water ($mol.dm^{-3}$)	Temperature in ˚K	Δ R_M	Temperature in ˚K	Δ R_M
0.0035	**298.15**	-0.0060	**308.15**	-0.0123
0.0105		-0.0124		-0.0143
0.0215		-0.0156		-0.0195
0.0365		-0.0125		-0.0290
0.0035	**303.15**	-0.0119	**313.15**	-0.0164
0.0105		-0.0139		-0.0144
0.0215		-0.0155		-0.0195
0.0365		-0.0188		-0.0314

The close perusal of present investigation shows that there is decrease in polarizability as well as molar refraction with increase in concentration of salts. This may be due to dispersion force. The cumulative dipole-dipole interaction may results in decrease in molar refraction and polarizability. Table No. 8 shows negative values of Δ R_M. The molar refraction values of $KBrO_3$ in 0.5% KNO_3 are smaller than $KBrO_3$ in water at all temperatures under investigation.

Conclusions:-

From the data it can be concluded that

1. The increase in densities with concentration may be due to strengthening of solute-solvent interactions.
2. The decrease in polarizability as well as molar refraction with increase in concentration of salts is due to dispersion force.
3. The decreasing magnitude of R_D indicates weak solute-solvent interactions.
4. The molar refraction values of $KBrO_3$in KNO_3, shows molar refraction is additive and constitutive property.

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