

STUDY OF MOLAR REFRACTION AND POLARISABILITY CONSTANT OF AQUEOUS SOLUTIONS OF KCl AND KBrO₃ AT DIFFERENT TEMPERATURES.

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Abstract: Densities and Refractive Indices of solutions of potassium bromate (KBrO₃) 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.

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 polarisability 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.

The present paper deals with the study of molar refraction and polarisability constant of KBrO₃ in aqueous KCl at different temperatures.

I. INTRODUCTION

The molar refractivity is a measure of the polarisability of the molecule[1]. The study of specific refractivity, molar refractivity and polarisability 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. This oxidation was recognized as friendly to the environment compared to the oxidation carried out by transition metal containing reagents such as chromate, permanganate, cerium and ruthenium salts. 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 SiO₂ 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]. Potassium bromate and Thio-glycolate are the two compounds used worldwide as hair curling solutions. The toxic effect of KBrO₃ 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]

II. EXPERIMENTAL

A. Materials

The chemicals (KCl and KBrO₃) were of high purity (ACS reagent ≥ 99.0%) obtained from Sigma Aldrich, used directly without further purification. Potassium bromate and potassium chloride are commercially available in the form of white crystals. Water used for solution preparation was triply distilled with specific conductance of $< 10^{-6} \text{S} \cdot \text{cm}^{-1}$. 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 KBrO₃ in KCl were prepared by diluting the stock solution. All weighing were done on electronic Contech balance having accuracy (0.0001g).

B. 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 $\pm 1.48 \times 10^{-4} \text{g} \cdot \text{cm}^{-3}$. The temperatures were measured with an uncertainty of $\pm 0.01^\circ\text{K}$.

C. 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.

III. DATA EVALUATION

The densities of solutions were determined from the relation as

$$d = M/V \quad \dots 1$$

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 [8-12].

$$E = n^2 \quad \dots 2$$

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

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

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

Where 'n' is refractive index of solutions, 'X_i' is the mole fractions of water, KCl and KBrO₃; 'M_i' is the molecular weights of water, KCl and KBrO₃; 'N' is Avogadro's number.

IV. 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 KBrO₃ 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 KBrO₃>KCl for the same concentration of the salt. This is due to relative salivation, 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 [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

- (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 $\Delta [R_M]$. 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]. The close perusal of present investigation shows that there is increase in polarizability as well as molar refraction with increase in concentration of salts. 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. Table No. 8 shows positive values of ΔR_M . The molar refraction values of KBrO₃ in 0.5% KCl are higher than in KBrO₃ in water at all temperatures under investigation.

V. CONCLUSIONS

From the data it can be concluded that

1. The higher values of densities of KBrO₃ than KCl are due to the relative salivation, 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 KBrO₃ in 0.5% KCl are higher than in KBrO₃ in water, shows molar refraction is additive as well as constitutive property.

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

Conc. of aqueous KCl in 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15°K						
0.1	0.99712	1.3326	1.7758	0.2061	3.7120	0.1472
0.2	0.99786	1.3327	1.7761	0.2060	3.7131	0.1472
0.3	0.99873	1.3329	1.7766	0.2059	3.7146	0.1473
0.4	0.99953	1.3331	1.7772	0.2058	3.7165	0.1474
0.5	1.00033	1.3332	1.7774	0.2057	3.7173	0.1474
303.15°K						
0.1	0.99572	1.3321	1.7745	0.2061	3.7111	0.1472
0.2	0.99673	1.3322	1.7749	0.2059	3.7122	0.1472
0.3	0.99746	1.3323	1.7750	0.2058	3.7133	0.1473
0.4	0.99826	1.3324	1.7753	0.2057	3.7141	0.1473
0.5	0.99931	1.3325	1.7756	0.2056	3.7145	0.1473
308.15°K						
0.1	0.99417	1.3313	1.7724	0.2059	3.7098	0.1471
0.2	0.99518	1.3314	1.7726	0.2058	3.7114	0.1471
0.3	0.99592	1.3316	1.7732	0.2058	3.7119	0.1472
0.4	0.99672	1.3317	1.7734	0.2056	3.7128	0.1472
0.5	0.99755	1.3319	1.7740	0.2056	3.7140	0.1473
313.15°K						
0.1	0.99250	1.3307	1.7708	0.2059	3.7089	0.1470
0.2	0.99350	1.3309	1.7713	0.2059	3.7108	0.1470
0.3	0.99438	1.3310	1.7716	0.2057	3.7116	0.1472
0.4	0.99518	1.3312	1.7721	0.2057	3.7124	0.1473
0.5	0.99616	1.3313	1.7724	0.2055	3.7136	0.1473

Table-2: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KBrO₃ 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15° K						
0.0035	0.99821	1.3325	1.7757	0.2058	3.7064	0.1469
0.0105	1.00023	1.3326	1.7758	0.2054	3.7032	0.1468
0.0215	1.00365	1.3327	1.7762	0.2048	3.6981	0.1467
0.0365	1.00844	1.3330	1.7769	0.2040	3.6915	0.1464
303.15° K						
0.0035	0.99712	1.3321	1.7746	0.2058	3.7063	0.1470
0.0105	0.99934	1.3322	1.7748	0.2054	3.7030	0.1468
0.0215	1.00261	1.3323	1.7750	0.2048	3.6977	0.1466
0.0365	1.00677	1.3324	1.7753	0.2040	3.6916	0.1464
308.15° K						
0.0035	0.99493	1.3313	1.7724	0.2058	3.7062	0.1469
0.0105	0.99719	1.3314	1.7726	0.2054	3.7026	0.1468
0.0215	1.00073	1.3315	1.7730	0.2047	3.6970	0.1466
0.0365	1.00557	1.3317	1.7737	0.2038	3.6899	0.1463
313.15° K						
0.0035	0.99338	1.3307	1.7708	0.2058	3.7060	0.1469
0.0105	0.99563	1.3308	1.7710	0.2053	3.7021	0.1468
0.0215	0.99929	1.3309	1.7713	0.2047	3.6958	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 Polarisability constant (α) of KBrO₃ in 0.1% KCl 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15° K						
0.0035	0.99838	1.3327	1.7762	0.2059	3.7105	0.1471
0.0105	1.00079	1.3328	1.7764	0.2054	3.7083	0.1470
0.0215	1.00465	1.3330	1.7768	0.2047	3.7005	0.1467
0.0365	1.00996	1.3332	1.7774	0.2038	3.6968	0.1464
303.15° K						
0.0035	0.99697	1.3322	1.7748	0.2059	3.7104	0.1471
0.0105	0.99932	1.3323	1.7750	0.2054	3.7066	0.1470
0.0215	1.00304	1.3324	1.7754	0.2048	3.7003	0.1467
0.0365	1.00810	1.3326	1.7758	0.2038	3.6945	0.1464
308.15° K						
0.0035	0.99538	1.3314	1.7727	0.2058	3.7102	0.1471
0.0105	0.99785	1.3315	1.7729	0.2053	3.7055	0.1469
0.0215	1.00179	1.3316	1.7732	0.2046	3.7000	0.1467
0.0365	1.00710	1.3318	1.7737	0.2036	3.6934	0.1463

313.15°K

0.0035	0.99333	1.3308	1.7711	0.2058	3.7100	0.1471
0.0105	0.99599	1.3309	1.7713	0.2056	3.7039	0.1469
0.0215	1.00017	1.3310	1.7717	0.2046	3.6996	0.1467
0.0365	1.00595	1.3312	1.7721	0.2036	3.6926	0.1462

Table-4: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KBrO₃ in 0.2% KCl 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15°K						
0.0035	0.99951	1.3328	1.7764	0.2057	3.7100	0.1472
0.0105	1.00181	1.3329	1.7766	0.2053	3.7063	0.1470
0.0215	1.00546	1.3331	1.7770	0.2046	3.7005	0.1467
0.0365	1.01044	1.3333	1.7776	0.2037	3.6928	0.1464
303.15°K						
0.0035	0.99779	1.3323	1.7751	0.2058	3.7099	0.1472
0.0105	1.00022	1.3324	1.7753	0.2053	3.7059	0.1470
0.0215	1.00399	1.3325	1.7757	0.2046	3.7001	0.1467
0.0365	1.00924	1.3327	1.7761	0.2036	3.6921	0.1464
308.15°K						
0.0035	0.99648	1.3315	1.7730	0.2056	3.7098	0.1471
0.0105	0.99873	1.3316	1.7732	0.2052	3.7055	0.1469
0.0215	1.00236	1.3318	1.7736	0.2045	3.6998	0.1467
0.0365	1.00730	1.3320	1.7742	0.2036	3.6914	0.1464
313.15°K						
0.0035	0.99471	1.3310	1.7716	0.2057	3.7097	0.1471
0.0105	0.99708	1.3311	1.7718	0.2053	3.7051	0.1469
0.0215	1.00091	1.3312	1.7722	0.2045	3.6991	0.1467
0.0365	1.00611	1.3314	1.7726	0.2035	3.6907	0.1463

Table-5: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KBrO₃ in 0.3% KCl 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15°K						
0.0035	1.00099	1.3330	1.7769	0.2055	3.7094	0.1471
0.0105	1.00318	1.3331	1.7772	0.2051	3.7062	0.1470
0.0215	1.00659	1.3333	1.7776	0.2045	3.7012	0.1468
0.0365	1.01111	1.3335	1.7782	0.2037	3.6951	0.1465
303.15°K						
0.0035	0.99935	1.3324	1.7754	0.2055	3.7091	0.1471
0.0105	1.00156	1.3325	1.7757	0.2051	3.7058	0.1470
0.0215	1.00495	1.3327	1.7761	0.2045	3.7003	0.1468
0.0365	1.00948	1.3329	1.7766	0.2037	3.6930	0.1465

308.15°K						
0.0035	0.99753	1.3317	1.7735	0.2055	3.7088	0.1471
0.0105	0.99984	1.3318	1.7738	0.2051	3.7054	0.1469
0.0215	1.00340	1.3319	1.7741	0.2044	3.6995	0.1467
0.0365	1.00849	1.3321	1.7745	0.2035	3.6906	0.1464
313.15°K						
0.0035	0.99638	1.3311	1.7719	0.2054	3.7084	0.1470
0.0105	0.99871	1.3312	1.7721	0.2050	3.7048	0.1469
0.0215	1.00240	1.3314	1.7725	0.2043	3.6988	0.1466
0.0365	1.00735	1.3316	1.7732	0.2034	3.6897	0.1463

Table-6: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KBrO₃ in 0.4% KCl 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15°K						
0.0035	1.00198	1.3332	1.7775	0.2054	3.7106	0.1472
0.0105	1.00409	1.3333	1.7778	0.2050	3.7077	0.1470
0.0215	1.00730	1.3335	1.7781	0.2045	3.7032	0.1469
0.0365	1.01169	1.3336	1.7785	0.2037	3.6967	0.1466
303.15°K						
0.0035	1.00061	1.3325	1.7757	0.2053	3.7094	0.1471
0.0105	1.00273	1.3327	1.7760	0.2049	3.7069	0.1470
0.0215	1.00603	1.3328	1.7764	0.2044	3.7014	0.1468
0.0365	1.01055	1.3330	1.7769	0.2035	3.6949	0.1465
308.15°K						
0.0035	0.99915	1.3318	1.7738	0.2052	3.7088	0.1470
0.0105	1.00120	1.3319	1.7740	0.2048	3.7051	0.1469
0.0215	1.00439	1.3320	1.7743	0.2043	3.6996	0.1467
0.0365	1.00899	1.3322	1.7748	0.2034	3.6925	0.1464
313.15°K						
0.0035	0.99736	1.3313	1.7724	0.2053	3.7078	0.1470
0.0105	0.99958	1.3314	1.7726	0.2049	3.7044	0.1468
0.0215	1.00309	1.3315	1.7729	0.2042	3.6977	0.1466
0.0365	1.00791	1.3317	1.7734	0.2034	3.6884	0.1462

Table-7: Density (d), Refractive index (n), Specific Refraction (R_D), Electronic polarization (E), Molar Refraction (R_M) and Polarisability constant (α) of KBrO₃ in 0.5% KCl 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)	Polarisability constant (α) × 10 ⁻²³ (cm ³ .mol ⁻¹)
298.15°K						
0.0035	1.00347	1.3334	1.7780	0.2052	3.7099	0.1471
0.0105	1.00538	1.3335	1.7782	0.2049	3.7073	0.1470
0.0215	1.00839	1.3336	1.7784	0.2043	3.7031	0.1469
0.0365	1.01235	1.3337	1.7788	0.2036	3.6981	0.1466

303.15°K						
0.0035	1.00218	1.3326	1.7759	0.2051	3.7085	0.1470
0.0105	1.00407	1.3327	1.7761	0.2047	3.7058	0.1469
0.0215	1.00705	1.3329	1.7765	0.2042	3.7009	0.1468
0.0365	1.01107	1.3331	1.7772	0.2035	3.6967	0.1466
308.15°K						
0.0035	1.00060	1.3320	1.7743	0.2050	3.7078	0.1470
0.0105	1.00260	1.3321	1.7745	0.2047	3.7047	0.1469
0.0215	1.00569	1.3322	1.7749	0.2041	3.6997	0.1467
0.0365	1.00991	1.3324	1.7753	0.2033	3.6939	0.1465
313.15°K						
0.0035	0.99857	1.3314	1.7727	0.2050	3.7073	0.1470
0.0105	1.00068	1.3315	1.7729	0.2047	3.7033	0.1468
0.0215	1.00400	1.3316	1.7732	0.2041	3.6969	0.1466
0.0365	1.00861	1.3318	1.7737	0.2033	3.6879	0.1462

Table-8: $\Delta [R_M]$ values for Molar Refraction of $KBrO_3$ in 0.5% KCl and Molar Refraction of $KBrO_3$ in water at different temperatures.

Concentration of $KBrO_3$ in water ($mol.dm^{-3}$)	Temperature in °K	ΔR_M	Temperature in °K	ΔR_M
0.0035	298.15	0.0035	308.15	0.0016
0.0105		0.0041		0.0021
0.0215		0.0050		0.0027
0.0365		0.0066		0.0040
0.0035	303.15	0.0022	313.15	0.0013
0.0105		0.0028		0.0012
0.0215		0.0032		0.0011
0.0365		0.0051		0.0006