



Effect of concentration on Ion Solvent Interactions and Thermo acoustic parameters of Barium chloride in mixed solvents at 303.15 K

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Abstract:

The thermo acoustical investigations for the ternary mixtures of barium chloride have been made in various diluents such as methanol, ethanol and 1,4-dioxane from ultrasonic velocity and density measurements at temperature 303.15K and atmospheric pressure. From these, isentropic compressibility(β_T), isothermal compressibility (β_s), Inter molecular free length(L_f), acoustic impedance(Z), molar sound velocity(R), molar compressibility(W) and coefficient of thermal expansion(α) have been calculated and interpreted in terms of ion-solvent interactions. The decrease in velocity and L_f with increase in concentration in all the systems indicates that there is a significant interaction between solute and solvent suggesting the structure promoting behaviour on addition of electrolyte. The interdependence of L_f and U has been evolved from model proposed by Eyring and Kincaid.

Key words: Ion-solvent interaction, Intermolecular free length, heat capacity ratio, Wada's constant, Rao's constant.

1. Introduction:

Barium chloride finds wide application in the laboratory. In industry, barium chloride is mainly used in the purification of brine solution in caustic chlorine plants and also in the manufacture of heat treatment salts, case hardening of steel, pigments and also used in fire-works to give a bright green colour. The aim of the research work is to create accurate data on thermodynamics and transport properties of solutions of barium chloride and to know more about the various types of interactions in solutions. Electrolytes dissolving in water have been classified as structure makers or structure breakers, depending on the charge density. It has been reported that ions with low charge density are net structure breakers; ions with a high charge density show an opposite behaviour and net structure makers. The intermolecular free length (L_f) is an important physical property of liquid mixtures which mainly affects the sound velocity. The intermolecular free length decreases with increase of concentration and hence the close packing of molecules which in effect increases the sound velocity [1, 2]. The isentropic compressibility (β_s) decreases with increase of velocity and gives insight into the structure making and structure breaking of components in binary mixtures [3]. A number of information about some physical properties [4] of the liquid such as internal pressure, intermolecular spacing, acoustic scattering, wave form distortion and structural behaviour, etc. can be obtained from the knowledge of this parameter. In fact there are extensive study of thermo dynamical property of electrolytes in aqueous or non aqueous solutions but very few in aqueous alcohol solutions. This paper reports density and ultrasonic velocity of barium chloride in methanol-water, ethanol-water and 1,4-Dioxane-water at 10% (v/v) composition mixture. The ultrasonic studies are extensively used



to estimate the thermodynamic properties and predict the intermolecular interactions of binary mixtures. The sound velocity is one of those physical properties that help in understanding the nature of liquid state. Using the measured values of sound velocity (U) and density (ρ), isentropic compressibility (β_s), isothermal compressibility (β_T), coefficient of thermal expansion (α), intermolecular free length (L_f), acoustic impedance (Z), molar sound velocity (R) and molar compressibility (W) can be computed. Such data are expected to highlight the role of electrolyte in presence of aqueous-organic solutions and its influence on concentration at a given temperature.

2. Material and Methods:

Methanol, ethanol, 1,4-Dioxane used were E. Merk "Extra Pure" variety. These were further purified by standard methods [5]. 10% v/v of each of methanol-water, ethanol-water and 1,4-dioxane-water was prepared in triply distilled deionised water. The mixtures were kept in special airtight bottles. Solutions of barium chloride were prepared by mass in an airtight Stoppard glass bottle. Masses were recorded on an electronic Dhona balance (India) with a precision of $\pm 1 \times 10^{-7}$ kg. The density (ρ) of barium chloride solutions were measured with the help of a double arm pycnometer. The uncertainty in density measurements was $\pm 1 \times 10^{-4}$ g cm⁻³. Ultrasonic velocities were measured by using a multifrequency ultrasonic interferometer (M-84, Mittal Enterprises, India) at 5 MHz. Uncertainty in ultrasonic velocity measurements were precise to ± 0.5 m s⁻¹. The ultrasonic interferometer was calibrated with triply distilled water. The temperature of the test liquids was maintained at 303.15 K to an accuracy of ± 0.01 K.

Density and ultrasonic velocities have been measured as a function of concentration (0.1 to 0.001) mol L⁻¹ and temperature 303.15 K at atmospheric pressure. Various thermo acoustical parameters have been evaluated from the experimentally measured values of density and ultrasonic velocity using following relations [6-13]:

$$\text{Isentropic compressibility } (\beta_s) = \frac{1}{\rho U^2} \dots\dots\dots (i)$$

$$\text{Isothermal compressibility } (\beta_T) = \frac{17.1 \times 10^{-4}}{T^{4/9} \rho^{4/3} U^2} \dots\dots\dots (ii)$$

$$\text{Coefficient of thermal expansion, } (\alpha) = \frac{75.6 \times 10^{-3}}{T^{1/9} U^{1/2} \rho^{1/3}} \dots\dots\dots (iii)$$

$$\text{Heat capacity ratio } (\gamma) = \frac{(\beta_T)}{(\beta_s)} \dots\dots\dots (iv)$$

$$\text{Intermolecular free length } (L_f) = K_T \times \beta_s^{1/2} \dots\dots\dots (v)$$

$$\text{Acoustic Impedance } (Z) = \rho U \dots\dots\dots (vi)$$



$$\text{Molar Sound Velocity } (R) = \left(\frac{M_z}{\rho} \right) U^{1/3} \dots\dots\dots \text{(vii)}$$

$$\text{Molar compressibility } (W) = \left(\frac{M_z}{\rho} \right) \beta_s^{-1/7} \dots\dots\dots \text{(viii)}$$

Where K_T is the Jacobson's temperature-dependent constant and is equal to $(93.875 + 0.375T) \times 10^{-8}$. And is equal to 207.5×10^{-8} at 303.15 K. M_z is the relative molar mass and T is temperature in Kelvin. R and W are also known as Rao's constant and Wada's constant respectively.

3. Results and Discussion:

3.1 Effect of Concentration of Solute:

The ultrasonic velocity and densities of BaCl_2 in aqueous solutions of methanol, ethanol and 1,4-dioxane at 303.15 K are presented in Table 1. Thermodynamic parameters such as isentropic compressibility (β_s), isothermal compressibility (β_T), inter molecular free length (L_f), acoustic impedance (Z), molar sound velocity (R), molar compressibility (W) and coefficient of thermal expansion (α) were calculated by using usual formula. The values are also given in Table 1 and 2. It is evident from Tables 1, that the values of density of barium chloride in mixed solvents increases with increase in concentration and changing the organic solvents from methanol to ethanol and 1,4-dioxane. Increase of concentration result in increase in number of particles in given region which leads shrinkage in volume of solution and hence density increases with increase of concentration. As density increases number of particles in given region is increased, this leads to quick transfer of sound velocity and hence ultrasonic velocity increases with increase of concentration. The increase in ultrasonic velocity indicates maximum association among the molecules of barium chloride solutions due to effective solute-solvent interaction. The increasing values of density and ultrasonic velocity reflect presence of strong interaction among the molecules of barium chloride solutions. The variation of U of system with concentration of BaCl_2 in mixed solvents can be expressed in terms of density and adiabatic compressibility by Eq. (ix)

$$dU/dc = U/2\rho \times d\rho/dc + 1/\beta_T \times d\beta_T/dc \quad \text{(ix)}$$

The sign and magnitude of quantity $d\rho/dc$ and $d\beta_T/dc$ indicate that the H-bonded structure of water is disrupted by the addition of BaCl_2 . Consequently, ultrasonic velocity of system increases depending on the structural properties of solute [14]. The solute that increases the ultrasonic velocity is of structure maker [15, 16] types. The electrolytes occupy the interstitial space of water and tend to break the original ordered state of water due to its self-association.

Adiabatic compressibility decreases with increase in concentration of electrolytes, a larger portion of the water molecules is electrostatic and the amount of bulk water decreases causing the compressibility to decrease. It is well known that solutes causing electrostriction lead to decrease in the compressibility of solution. Hydrophilic solutes often show negative compressibility as well [17], due to ordering that is induced by them in water structure. Negative value of $d\beta_s/dc$ in the present study indicates the electrostriction of water molecules (Fig.1 and 2).

Specific acoustic impedance is defined as the impedance offered to the sound wave by the components of mixture. Mathematically it is directly proportional to ultrasonic velocity and inversely proportional to that



of isentropic and isothermal compressibility and shows similar behaviour to that of ultrasonic velocity and opposite to that of compressibility. It is observed that the value of acoustic impedance (Z) increases in all solutions with increase in solute concentrations (Fig.6). This suggests increase in molecular packing in medium and it may further support strengthening of ionic interactions due to hydrogen bonding. The variation of ultrasonic velocity depends on the intermolecular free length (L_f) on mixing which is a predominant factor in determining the variation of ultrasonic velocity in fluids and in their solutions. It has been observed in the present study that intermolecular free length decreases with concentration of solute at 303.15 K as shown in Fig (5). The decrease in L_f with increase of solutes concentrations in solution indicates that there is a significant interaction between solute and solvent suggesting the structure promoting behaviour on addition of electrolyte. The interdependence of L_f and U has been evolved from model proposed by Eyring and Kincaid [18]. The decrease in the values of adiabatic compressibility and the free length with increase in ultrasonic velocity further strengthens the strong molecular association between the unlike molecules through hydrogen bonding.

The variation of coefficient of thermal expansion, α as shown in Fig.3 is found that these values decrease with increase in concentration of barium chloride. Such variation can be well explained on the basis of the fact that, the increase in concentration causes more ion-solvent interactions resulting in increase in the density values. The ultrasonic velocity also increases due to compactness and smaller intermolecular free length which decreases the values of α in a solution. This decrease in α , causes a decrease in the volume and so also in isentropic compressibility and isothermal compressibility. The heat capacity ratio of the binary mixtures are found to be decreased in a linear trend with the decrease in concentration of barium chloride (Fig.4), and its value varies from 1.34 to 1.36 which is well agreed with that of the result for other substances. Molar sound velocity (R), also known as Rao's constant, increases with increasing concentration (Fig.7) shows that there is strong interaction between solute and solvent molecules. Molar adiabatic compressibility (W), also known as Wada's constant may be considered for existing interaction. The values of W increases with increasing concentration (Fig.8) indicate that there must be tight packing of the medium and hence interaction is increasing [19].

3.2 Effect of Solvents:

It is also found that all the parameters discussed above are also affected by the presence of different solvents used in the solution. It is observed that the values of isentropic and isothermal compressibility, Coefficient of thermal expansion, Heat capacity ratio and Intermolecular free length of barium chloride is decreases in the order Methanol-Water > Ethanol-Water > 1,4-Dioxane -Water . The larger β values which show molecular association/interaction is greater in 10% 1,4-dioxane-water mixture than other two mixtures. $BaCl_2$ molecules exist in the ionic form and thus have stronger interaction with the surrounding water molecules. The increasing electrostrictive compression of water around the ions results in a large decrease in compressibility of solutions. The negative variation of both the profiles suggests that there is association of solvents leading to compression in volume and hence a decrease in isentropic and isothermal compressibility [20]. It may further support strengthening of ionic interactions due to hydrogen bonding. Since hydrogen bonding in 1,4-Dioxane-water > Ethanol-Water > Methanol-Water. Greater the H-bonding contract the volume of the solutions. Therefore the ultrasonic velocity is more in 1,4-dioxane - water than other two mixtures. Again the values of W , R and Z in different mixed solvents is in the order 1,4-dioxane-water > ethanol-water > methanol-water. Therefore the interaction is more in 1,4-dioxane-water.



4. Conclusion:

In the present study, experimental results for ultrasonic velocity, density are reported for barium chloride in aqueous solution of methanol, ethanol and 1,4-dioxane. The increasing trend in ultrasonic velocity, density with increasing the concentration of solute suggests that a molecular interaction exists between solute and solvent molecules. The H-bonded structure of water is disrupted by the addition of BaCl₂. The electrolytes occupy the interstitial space of water and tend to break the original ordered state of water. Interaction between solute and solvent molecules results in decrease in free length, L_f and increase in density and velocity with increase of solute concentration.

Decreasing trend of Z , R and W indicate the compactness in solution and structure making ability of barium chloride with strong ion solvent interactions in aqueous organic solvents. Compressibility β_s , β_T decreases with increase in concentration. A large portion of the water molecule exerts electrostatic force which attracts the neighbouring molecules decreasing the effective volume of water. This leads to the decrease in compressibility. On the basis of the above discussion it can be concluded that the variation of different thermo acoustic parameters not only affected by the variation pressure and temperature but also with the concentration of electrolyte and the nature of solvents used.

Table-1 :Experimentally determined ultrasonic velocity, U , density, ρ , and calculated values of isentropic compressibility, (β_s) isothermal compressibility, (β_T) co-efficient of thermal expansion, (α), heat capacity reties, (γ) Intermolecular Free length, (L_f) of barium chloride solution in 10% Methanol - water, 10% Ethanol - water & 10% 1,4-Dioxane - water at 303.18K.

c/molL^{-1}	ρ/kgm^{-3}	U/ms^{-1}	$\beta_s \times 10^{10}/\text{m}^2\text{N}^{-1}$	$\beta_T \times 10^{15}/\text{m}^2\text{N}^{-1}$	$\alpha \times 10^4/\text{K}^{-1}$	$\gamma \times 10^5$	$L_f \times 10^{11}/\text{m}$
BaCl ₂ in 10 % Methanol-Water							
0.1	997.2	1555	4.1472	5.6000	1.0170	1.3503	4.22683
0.075	993.8	1554	4.1668	5.6329	1.0184	1.3518	4.23677
0.05	990.3	1553	4.1869	5.6668	1.0200	1.3534	4.24699
0.025	986.8	1551.5	4.2099	5.7046	1.0217	1.355	4.25863
0.01	984.7	1550.5	4.2243	5.7282	1.0227	1.356	4.26591
0.0075	984.3	1550	4.2287	5.7350	1.0230	1.3562	4.26816
0.005	984.0	15495	4.2327	5.7410	1.0233	1.3563	4.27018
0.0025	983.6	1549.5	4.2399	5.7441	1.0234	1.3567	4.27105
0.001	983.4	1548	4.2435	5.7568	1.0240	1.3566	4.27563
0.000	983.3	1547	4.2495	5.7651	1.0244	1.35665	4.27861



BaCl ₂ in 10 % Ethanol-Water							
0.1	998.7	1567	4.0435	5.5184	1.0132	1.3474	4.1955
0.075	995.2	1566.4	4.1171	5.5337	1.0139	1.3499	4.2002
0.05	991.7	1565	4.0953	5.5697	1.0156	1.3525	4.2114
0.025	988.2	1563.8	4.1380	5.6046	1.0172	1.3544	4.2221
0.01	986.1	1562	4.1564	5.6335	1.0185	1.3553	4.2315
0.0075	985.7	1561	4.1634	5.6438	1.0189	1.3555	4.2350
0.005	985.3	1560	4.1704	5.6540	1.0194	1.3557	4.2386
0.0025	984.9	1558	4.1829	5.6717	1.0202	1.3559	4.2449
0.001	984.7	1556.5	4.1918	5.6842	1.0207	1.356	4.2494
0.000	984.6	1555	4.2003	5.6959	1.0213	1.356	4.2537
BaCl ₂ in 10% 1,4-Dioxane - water							
0.1	1027.6	1564	3.9783	5.3186	1.0039	1.3369	4.1398
0.075	1024.1	1563	3.9971	5.3497	1.0054	1.3383	4.1495
0.05	1020.5	1562	4.0163	5.3817	1.0069	1.3399	4.1595
0.025	1016.9	1561	4.0357	5.4141	1.0084	1.3415	4.1695
0.01	1014.8	1560	4.0492	5.4360	1.0094	1.3424	4.1765
0.0075	1014.4	1559.5	4.0534	5.4423	1.0097	1.3426	4.1787
0.005	1014.0	1558	4.0628	5.4557	1.0103	1.3428	4.1835
0.0025	1013.7	1556	4.0745	5.4719	1.0111	1.3429	4.1895
0.001	1013.5	1555	4.0805	5.4804	1.0115	1.3430	4.1927
0.000	1013.3	1554	4.0866	5.4888	1.0119	1.3431	4.1958

c/molL^{-1}	$Z \times 10^{-6} / \text{kg m}^{-2} \text{sec}^{-1}$	$R / (\text{m}^3/\text{mol})(\text{m/s})^{1/3}$	$W / (\text{m}^3/\text{mol})(\text{N/m}^2)^{1/7}$
BaCl₂ in 10% Methanol- Water			
0.1	1.550646	0.257449	0.487714
0.075	1.544365	0.248252	0.470076
0.05	1.537936	0.238566	0.451521
0.025	1.531020	0.228884	0.432998
0.01	1.526777	0.222991	0.421734
0.0075	1.525665	0.221991	0.419824
0.005	1.524708	0.220979	0.417898
0.0025	1.524088	0.218839	0.413827
0.001	1.522303	0.217897	0.413554
0.000	1.521165	0.218893	0.413044
BaCl₂ in 10% Ethanol - Water			
0.1	1.561829	0.261888	0.495908
0.075	1.558881	0.251924	0.476946
0.05	1.552011	0.242262	0.458443
0.025	1.545347	0.232466	0.439699
0.01	1.540288	0.226439	0.428193
0.0075	1.538678	0.225403	0.426221
0.005	1.537068	0.224366	0.424249
0.0025	1.534474	0.223293	0.422221
0.001	1.532686	0.222621	0.420957
0.000	1.531053	0.222138	0.420056

BaCl ₂ in 10% 1,4-Dioxane - water			
0.1	1.607166	0.261604	0.49758
0.075	1.600668	0.252336	0.479733
0.05	1.594021	0.24293	0.461633
0.025	1.587381	0.233372	0.443258
0.01	1.583088	0.227523	0.432035
0.0075	1.581957	0.226528	0.430128
0.005	1.579812	0.225507	0.428184
0.0025	1.577317	0.224417	0.426122
0.001	1.575993	0.223979	0.425293
0.000	1.574668	0.223349	0.424096

Figures

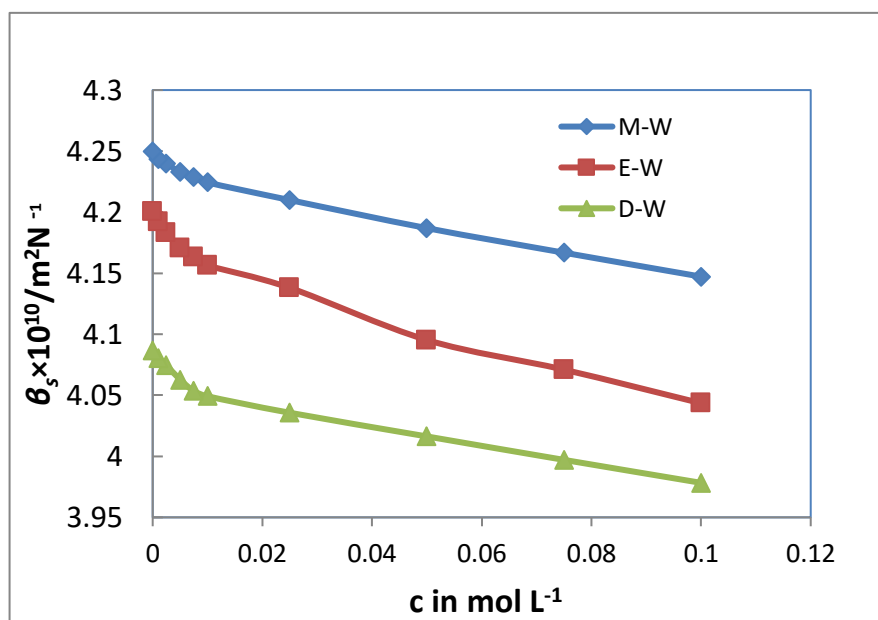


Figure 1: Plot of β_s against concentration of Barium Chloride in 10% Methanol + Water, 10% Ethanol + Water, 10% 1,4-dioxane - water at 303.15 K

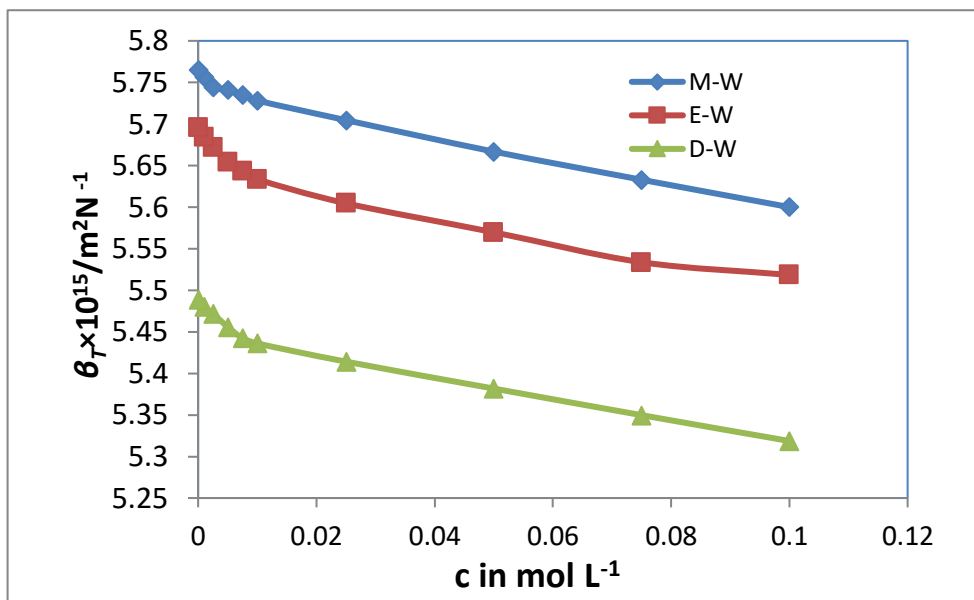


Figure 2: Plot of β_r against concentration of Barium Chloride, in 10% Methanol + Water , 10% Ethanol + Water and 10% 1,4-dioxane - water at 303.15K

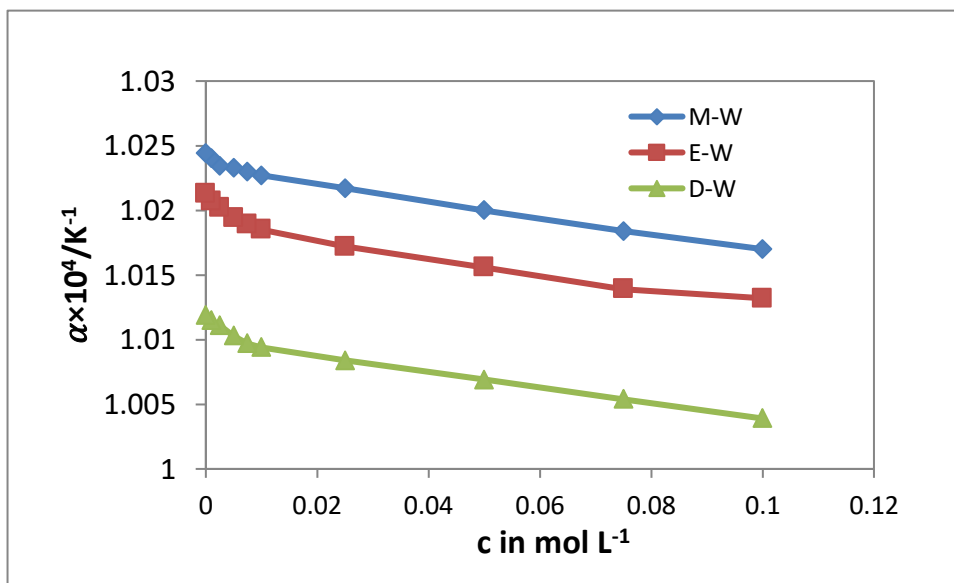


Figure 3: Plot of α against concentration of Barium Chloride in 10% Methanol + Water , 10% Ethanol + Water , 10% 1,4-dioxane - water at 303.15K

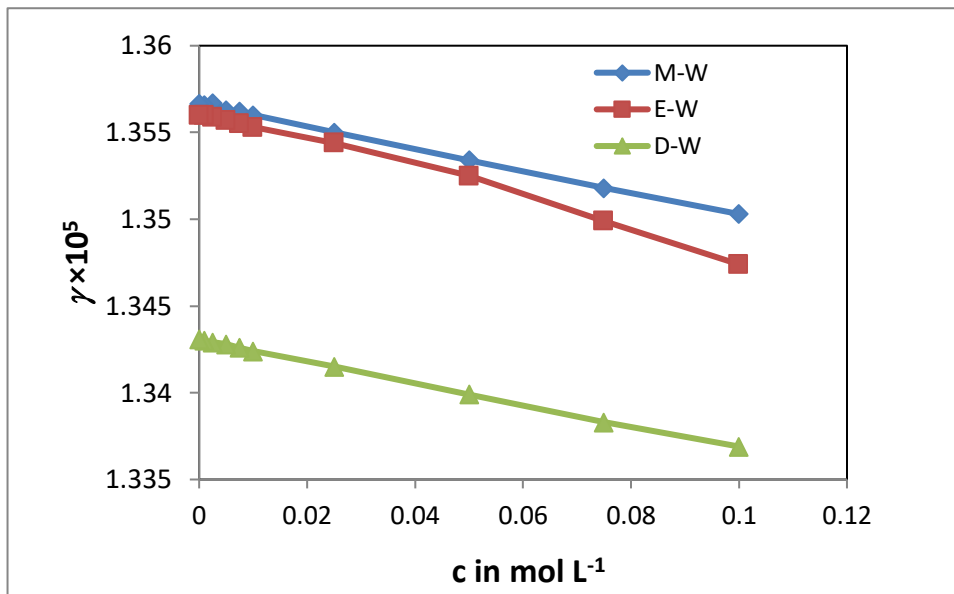


Figure 4: Plot of γ against concentration of Barium Chloride in 10% Methanol + Water , 10% Ethanol + Water and 10% 1,4-Dioxane - water at 303.15 K

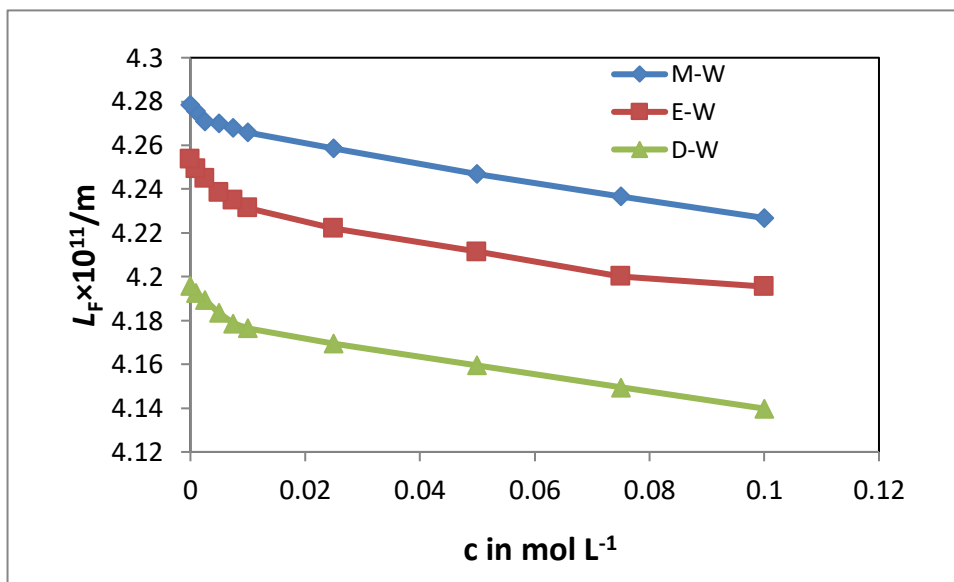


Figure 5: Plot of L_f against concentration of Barium Chloride in 10% Methanol + Water , 10% Ethanol + Water and 10% 1,4-dioxane - water at 303.15 K

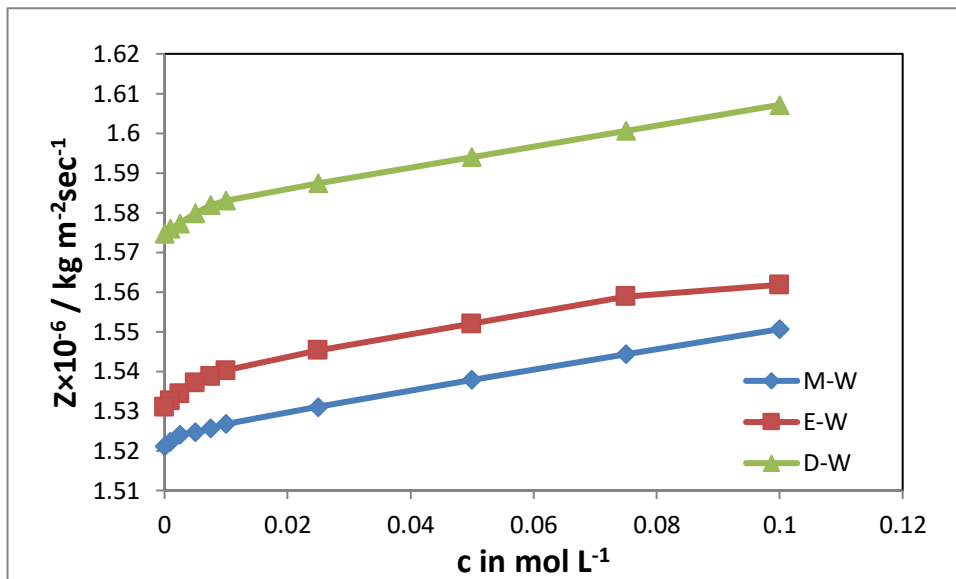


Figure 6: Plot of Z against concentration of Barium Chloride in 10% Methanol + Water , 10% Ethanol + Water and 10% 1,4-dioxane - water at 303.15 K

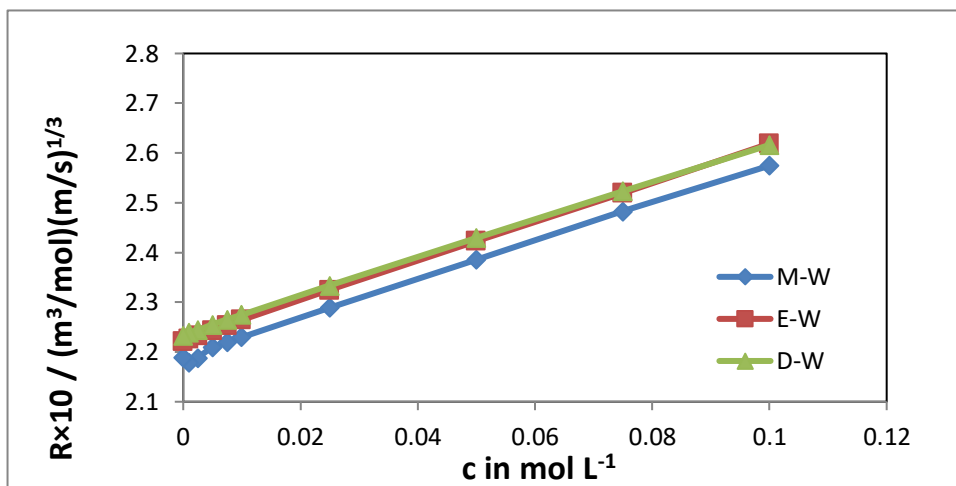


Figure 7: Plot of R against concentration of Barium Chloride in 10% Methanol + Water , 10% Ethanol + Water and 10% 1,4-dioxane - water at 303.15 K

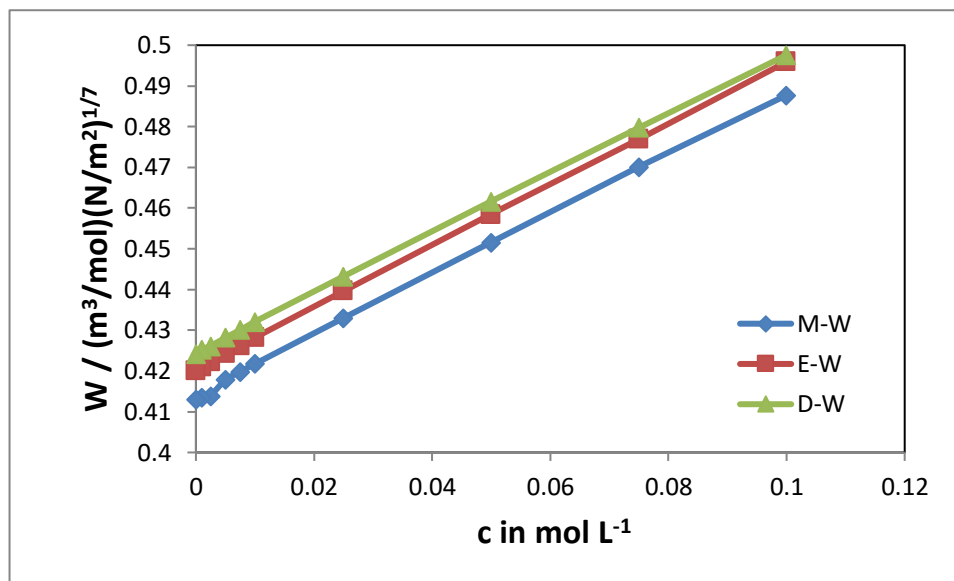


Figure 8: Plot of W against concentration of Barium Chloride in 10% Methanol + Water, 10% Ethanol + Water and 10% 1,4-dioxane + Water at 303.15 K

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