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INTERMOLECULAR INTERACTIONS IN AQUEOUS SOLUTION OF POLYVINYL ALCOHOL

Richa Saxena*[1] and S. C. Bhatt[2]
[1]IFTM University, Lodhipur, Rajput, Moradabad-244001, (Uttar Pradesh) India
[2]Ultrasonic and Dielectric Laboratory, Department of Physics, H.N.B. Garhwal University, Srinagar-246174, Garhwal, (Uttarakhand) India
*E-mail saxena.richa23@gmail.com

ABSTRACT
Density, viscosity, and ultrasonic velocity studies have been carried out in an aqueous solution of poly vinyl alcohol at 1 MHz frequency. Measurements were carried out in temperature range 30ºC to 65ºC at different concentration range 0.3% to 1.0%. From these different acoustical parameters have been calculated from intermolecular free length and relaxation time by using measured values of ultrasonic speed, density, and viscosity. By using these values intermolecular interactions and relaxation time are discussed.
Keywords: Ultrasonic velocity, intermolecular free length, relaxation time

INTRODUCTION
For many years ultrasonic has been used in a variety of fields such as biology, biochemistry, dentistry, engineering, geography, geology, industry, medicine, polymers[1].Ultrasonic studies have found wide applications owing to their ability to characterize the physic-chemical behavior of solutions. The measurement of ultrasonic velocity can provide useful information regarding the degree of deviation from ideality, internal structure, complex formation and molecular interaction in liquids[2]. Ultrasonic waves can propagate through matter and therefore they can be used for detecting the discontinuities present in a cast or forged materials[3]. The volumetric properties of binary liquid mixtures have been extensively studied [4-7], as they can contribute to a clarification of the various intermolecular interactions between the different species existing in solution. Polyvinyl alcohol is interesting from several aspects. It is one of the simplest of the synthetic water-soluble polymers. Commercially polyvinylalcohol is synthesized by the hydrolysis of polyvinyl acetate, since hydrolysis is difficult to take to completion a number of completion a number of partially hydrolyzed polymers containing residual acetate groups carry the name of PVA.[8-10]Polymer dissolution play also plays a key role in many industrial applications in many industrial applications in a variety of areas and an understanding of the dissolution process allows for the optimization of design and processing conditions as well as selection of suitable solvent.[11]There have been a number of reports on acoustics, dielectric, refractometric, volumetric, thermodynamic properties of binary liquid mixtures consisting of associated, associated-non-associated and non-associated and nonassociated compounds[12].

EXPERIMENTAL
In the present investigation polyvinyl alcohol in the solid form of molecular weight, approximately 140,000 is used. The solutions were prepared by adding known volume of polyvinyl alcohol to fixed volume of water and stirring under reflex, until a clear solution was obtained. The concentration range studied in the solution is 0.3%- 1.0% (v/v). Different acoustical parameters like, intermolecular free length and relaxation time were calculated at different concentration like 1.0%, 0.8%, 0.6%, 0.5%, 0.4% and 0.3% and at different temperatures 30ºC, 35˚C, 40˚C, 45˚C, 50˚C, 55˚C, 60˚C and 65˚C at 1MHz frequency by using variable path ultrasonic interferometer with reproducibility of ±0.4m/s at 25^0C. The temperature of the solution has been kept constant by circulating water from the thermostatically

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controlled (±0.1^{0}C) water bath. The densities at different temperatures were measured using 10ml specific gravity bottle and single pan macro balance. The uncertainty in density measurements was found to be about 0.5kg/m^3. The viscosity of the mixtures was determined by using Ostwald's viscometer, which was kept inside a double-walled –jacket, in which water from thermostat water bath was circulated. The inner cylinder of this double-wall-glass jacket was filled with water of the desired temperature so as to establish and maintain the thermal equilibrium. The accuracy of the viscosity measurements is within ±0.5%. These parameters are calculated by using standard relations.[11-14]

RESULTS AND DISCUSSION

In the present work density, viscosity and ultrasonic velocity have been measured at different temperature and concentration of polyvinyl alcohol, which is shown in Table-1, 2, and 3 respectively. By using these values for PVA, intermolecular free length and relaxation time have been calculated by using well-known relations and the results have been presented in Table-4 and 5, respectively. The variations of these parameters with temperature and concentration have been shown in Fig.-1 to Fig.-6 respectively.

Polyvinyl alcohol in the solid form of molecular weight 140,000 is used. The solution was prepared by adding the known weight of the polyvinyl alcohol of molecular weight approximately 140,000 to a fixed volume of water and stirring under reflex, until a clear solution was obtained. Table-1 and Fig.1& 2 represent the variation of density with temperature and concentration respectively. Density decreases with increase in temperature and increases with increase in concentration. These are in agreement with earlier workers[15]. It may be due to electro striction in that solution. This electro striction decreases the volume and hence increases the density as a number of solute molecules increase the electro striction and density.

Table-1: Density(x10^{3}kg/m^3) of polyvinyl alcohol (PVA) at different temperature and concentration at 1 MHz frequency

Temperature Concentration	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	55^{0}C	60^{0}C	65^{0}C
1.0%	1.020	0.996	0.992	0.988	0.983	0.979	0.974	0.968
0.8%	0.985	0.983	0.981	0.979	0.977	0.972	0.964	0.956
0.6%	0.981	0.978	0.974	0.972	0.968	0.96	0.954	0.948
0.5%	0.978	0.975	0.971	0.968	0..963	0.958	0.946	0.937
0.4%	0.976	0.973	0.969	0.965	0.955	0.950	0.939	0.934
0.3%	0.974	0.970	0.967	0.962	0.951	0.944	0.931	0.926

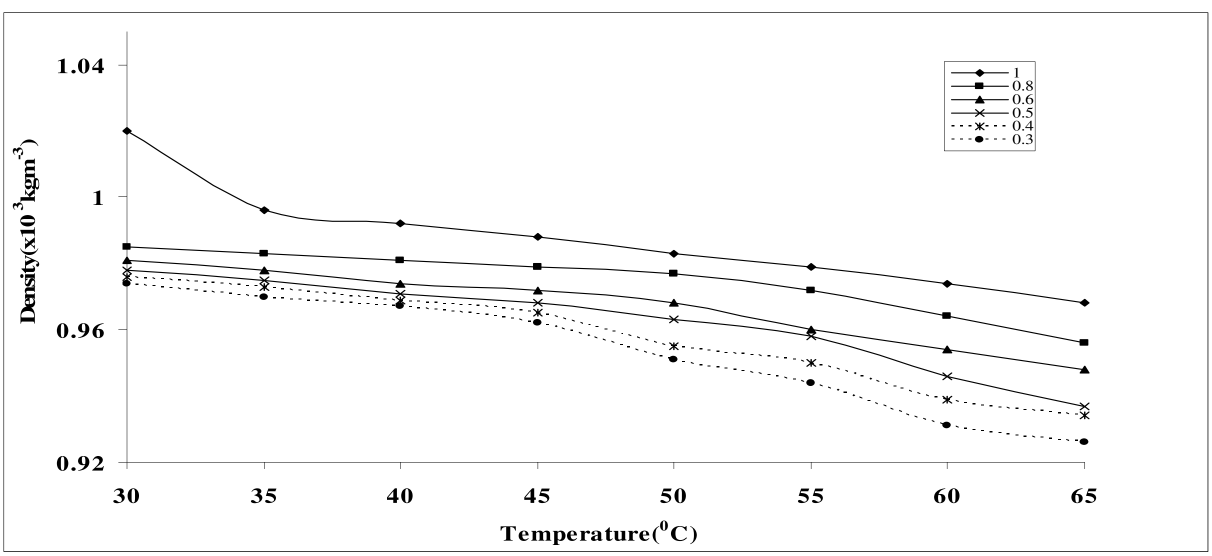

Fig.-1: Variation of density with temperature at different concentration of PVA

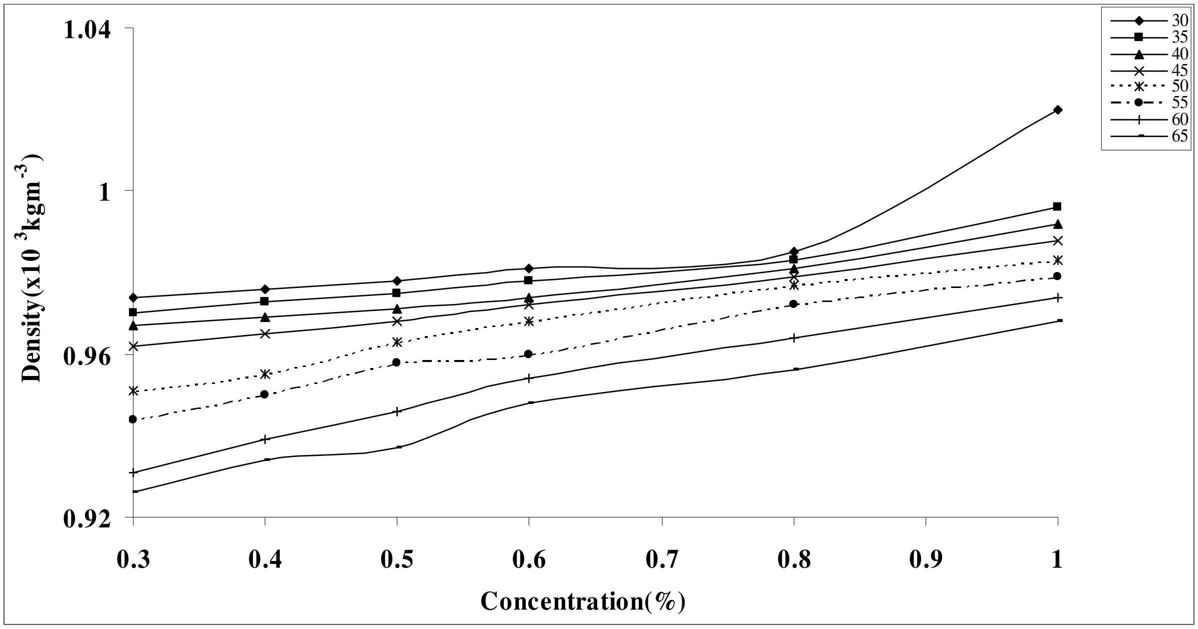

Fig.-2: Variation of density with concentration with at different temperature of PVA

Table-2: Viscosity (x10^{-1}Pa.s) of polyvinyl alcohol (PVA) at different temperature and concentration at 1 MHz frequency

Temperature Concentration	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	55^{0}C	60^{0}C	65^{0}C
1.0%	0.092	0.089	0.087	0.085	0.082	0.079	0.062	0.058
0.8%	0.090	0.086	0.084	0.081	0.078	0.069	0.059	0.056
0.6%	0.089	0.077	0.067	0.061	0.056	0.052	0.044	0.041
0.5%	0.087	0.074	0.065	0.059	0.054	0.047	0.042	0.038
0.4%	0.083	0.073	0.064	0.057	0.051	0.043	0.038	0.035
0.3%	0.078	0.072	0.060	0.054	0.048	0.042	0.330	0.310

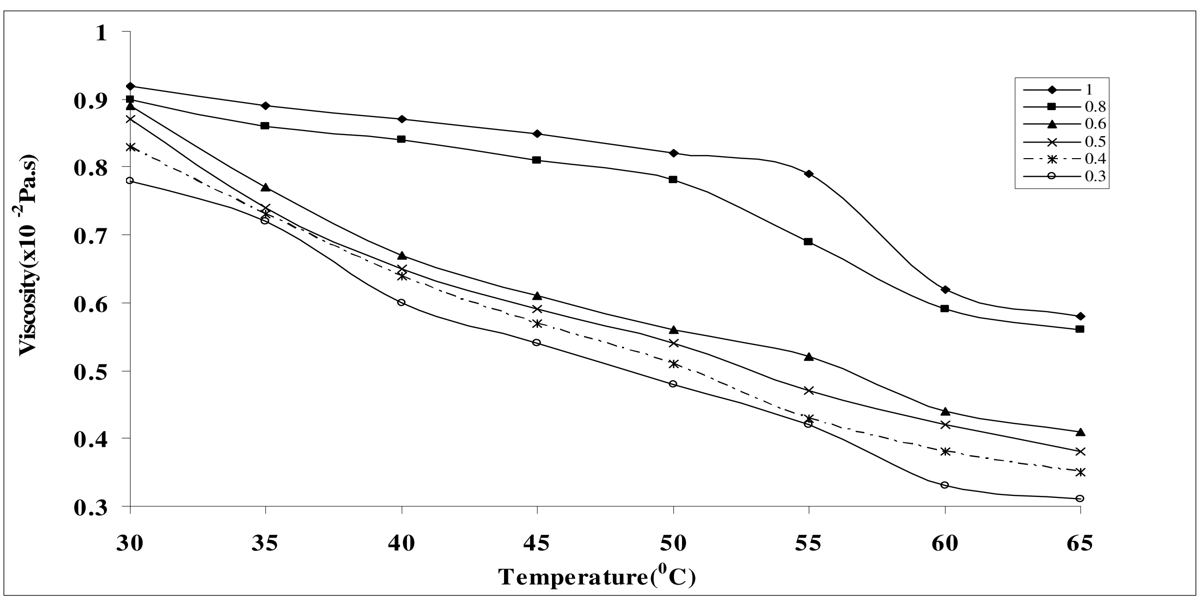

Fig.-3: Variation of viscosity with temperature at different concentration of PVA

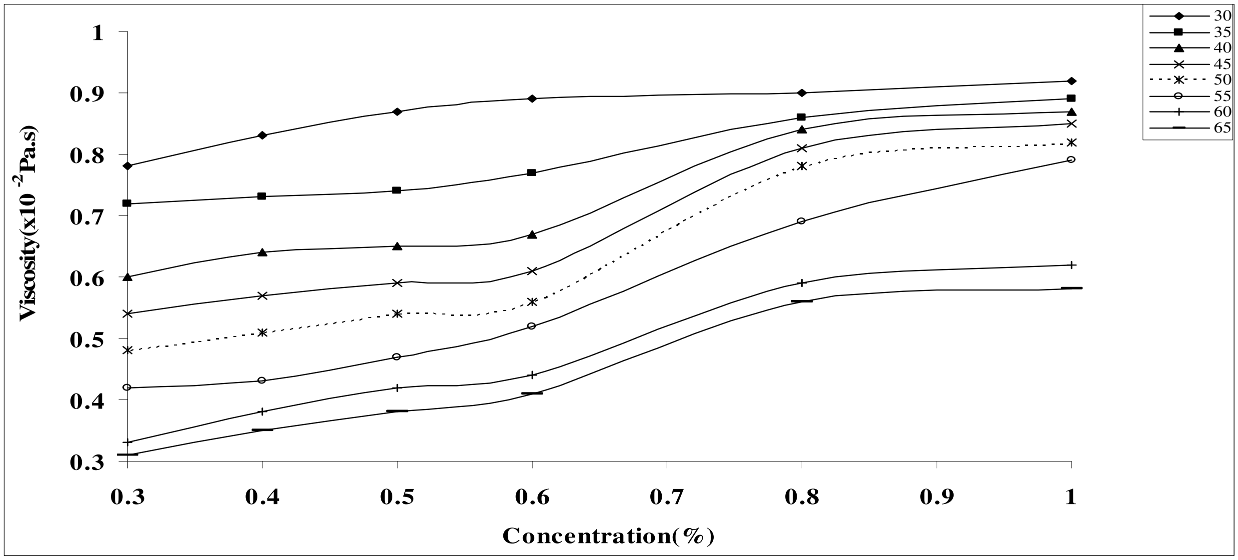

Fig.-4: Variation of viscosity with concentration at different temperature of PVA

Table- 3: Ultrasonic velocity (m/s) of polyvinyl alcohol (PVA) at different temperature and concentration at 1 MHz frequency

Temperature concentration	30^0C	35^0C	40^0C	45^0C	50^0C	55^0C	60^0C	65^0C
1%	1512.2	1509.9	1504.2	1501	1495.6	1482.5	1476.5	1472.3
.8%	1507.6	1503.2	1500.1	1498.8	1488.7	1473.	1470.6	1467.7
.6%	1505.1	1501.3	1497.5	1484.4	1472.7	1468.8	1463.7	1461.8
.5%	1502.4	1495.9	1482.3	1476.7	1468.9	1466.8	1463.7	1461.9
.4%	1496.5	1483.8	1480.8	1473.5	1466.7	1464.6	1460.3	1458.9
.3%	1493.7	1482.5	1478.4	1472.3	1462.6	1459	14566.2	1454.8

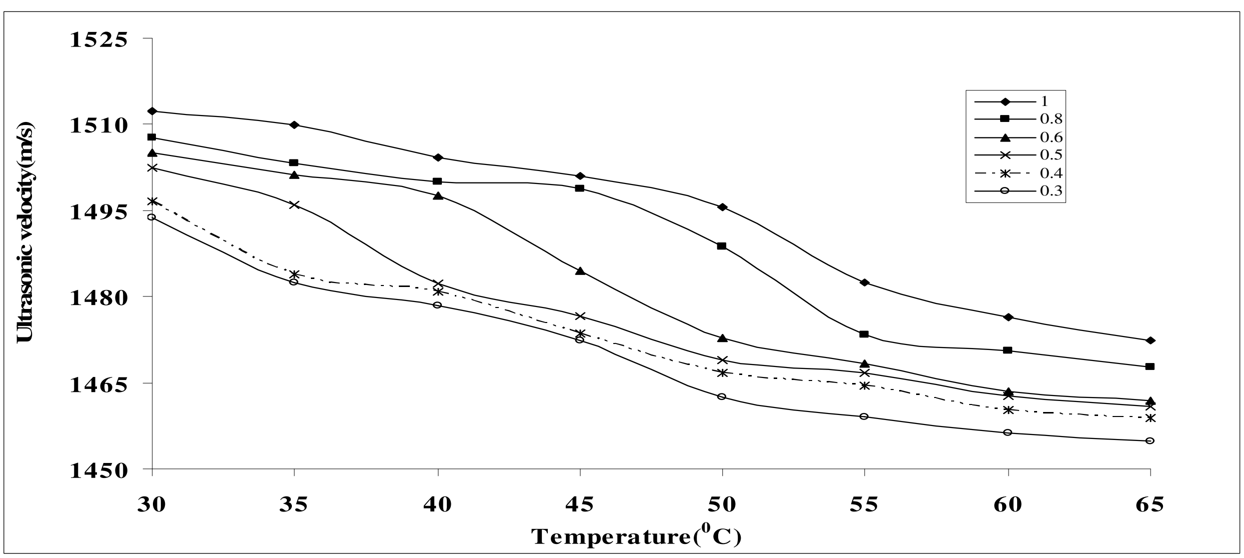

Fig.-5: Variation of ultrasonic velocity with temperature at different concentration of PVA

It is evident from Table-2 and Fig.-3 and 4 that, viscosity decreases with increase in temperature and increases with increase in the concentration of PVA. This is showing a similar trend as reported by earlier workers[16, 17].The variations of ultrasonic velocity with temperature and concentration have been shown in Table-3 and Fig.-5 and 6. Ultrasonic velocity decreases with increase in temperature and increases with increase in the concentration of PVA. A similar result has been reported by earlier workers[18]. This indicates interactions between PVA and solvent molecules. The increase or decrease in value of ultrasonic velocity and intermolecular free length with composition indicates interactions between contributing molecules. As per the model of Eyring and Kincaid[19] for sound propagation, ultrasonic velocity increases on the decrease of free length.

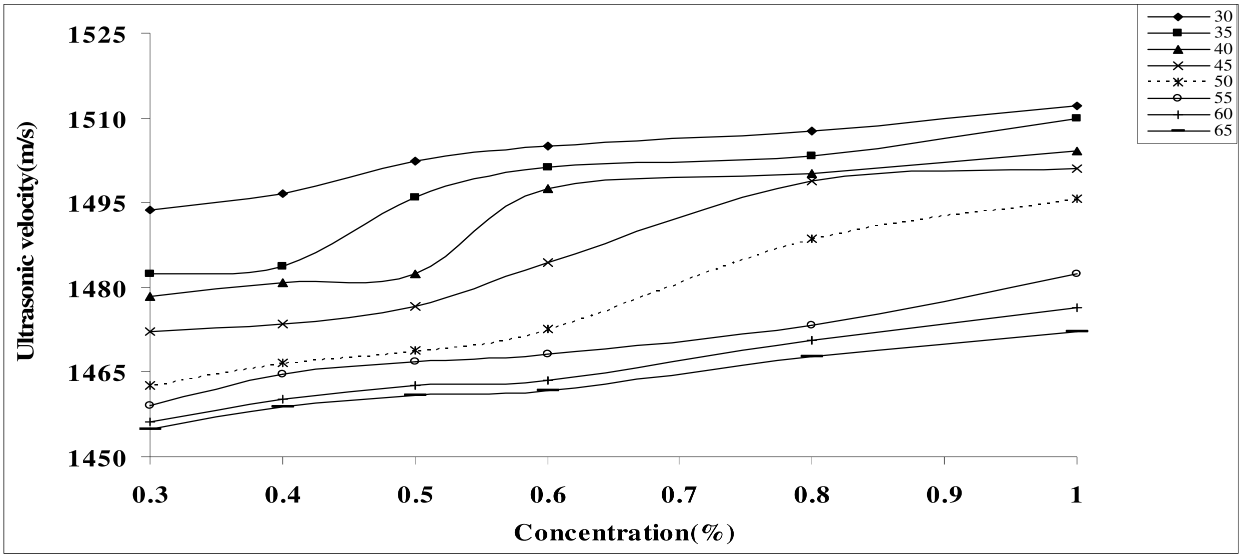

Fig.-6: Variation of ultrasonic velocity with concentration at different temperature of PVA

Intermolecular free length is a predominant factor as it determines the sound velocity in the condensed and fluid state. The increase in the solute concentration leads to the decrease in the gap between two species and this is ideally observed in present work.

Table-4: Intermolecular Free Length (x10^{-13}m) at different temperature and concentration at 1MHz for polyethylene glycol (PEG)

Temperature concentration	30^0C	35^0C	40^0C	45^0C	50^0C	55^0C	60^0C	65^0C
1.0%	2.802	2.84	2.857	2.869	2.886	2.918	2.937	2.955
.8%	2.861	2.872	2.881	2.886	2.909	2.946	2.964	2.983
.6%	2.871	2.883	2.896	2.925	2.954	2.975	2.994	3.007
.5%	2.881	2.898	2.936	2.946	2.969	2.981	3.006	3.025
.4%	2.895	2.924	2.954	2.957	2.986	2.998	3.025	3.036
.3%	2.903	2.931	2.944	2.964	3.001	3.019	3.046	3.057

It is clear from Fig.-7 and Table-4 that intermolecular free length increases with increase in temperature and decreases with increase in concentration (Fig.-8). It is similar trend reported by earlier workers. This is also in accordance with the expected molecular interaction between the solute-solvent, increases in compressibility.

It is clear from Table-5, and Fig.-9 and 10 Relaxation time decrease with increase in temperature and increases with increase in concentration. This may be due to structural relaxation process.[20] And in such situation, it is suggested that molecules get arranged due to cooperative process.[21] This trend is quite normal as the variation in these parameters is the cumulative effect of the variations in density, viscosity and ultrasonic velocity of the solutions under the given condition. This may be due to as per the kinetic theory of fluid.

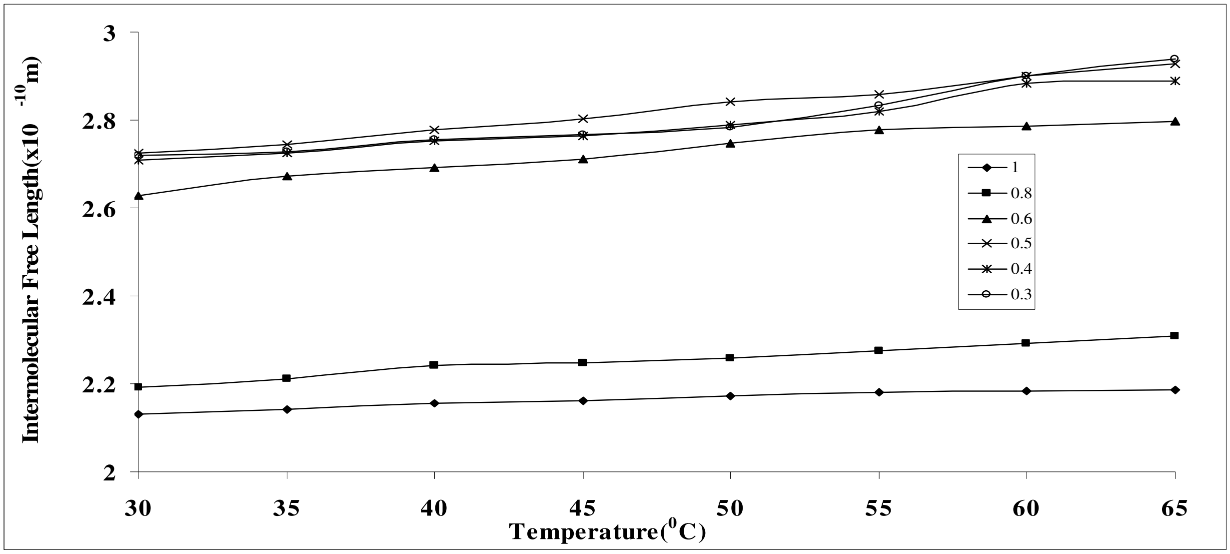

Fig.-7: Variation of Intermolecular Free Length (x10-13m)with temperature at different concentration of PVA

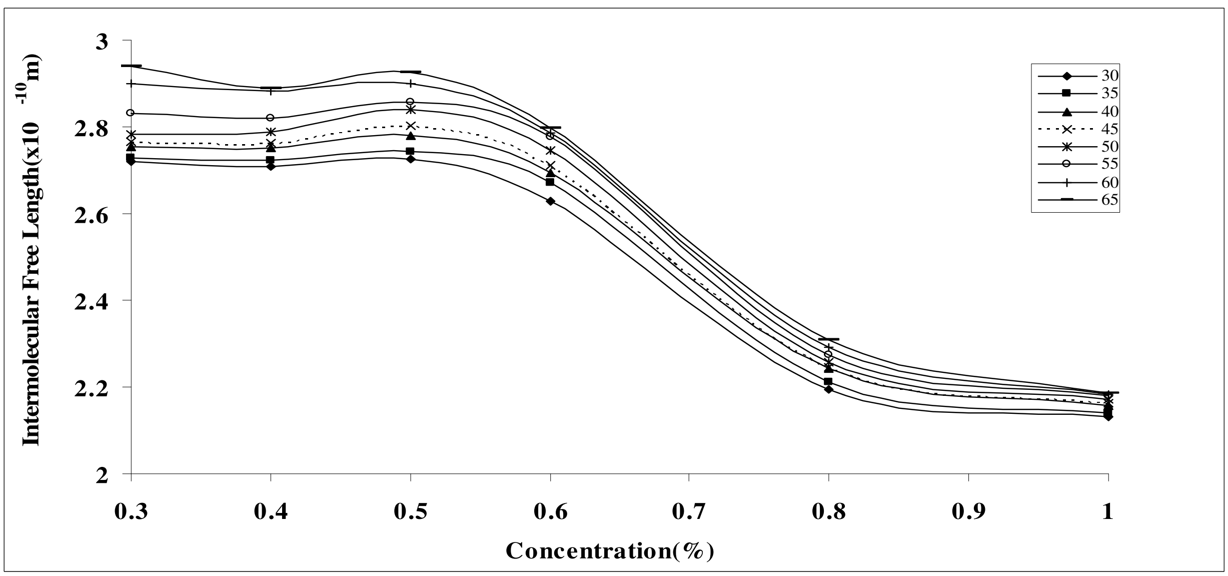

Fig.-8: Variation of Intermolecular Free Length (x10^{-13}m)with concentration at different temperature of PVA

Table- 5: Relaxation time (x10-12s) at different temperature and concentration at 1MHz for polyethylene glycol (PEG)

Temperature Concentration	30^{0}C	35^{0}C	40^{0}C	45^{0}C	50^{0}C	55^{0}C	60^{0}C	65^{0}C
1%	2.11	2.00	1.79	1.57	1.35	1.20	0.844	0.696
.8%	2.06	1.54	1.07	0.998	0.868	0.727	0.615	0.609
.6%	1.78	1.32	1.02	0.974	0.856	0.803	0.728	0.61
.5%	1.46	1.25	0.802	0.589	0.528	0.522	0.507	0.51
.4%	1.36	0.799	0.595	0.533	0.483	0.449	0.423	0.318
.3%	0.63	0.504	0.44	0.407	0.389	0.368	0.338	0.334

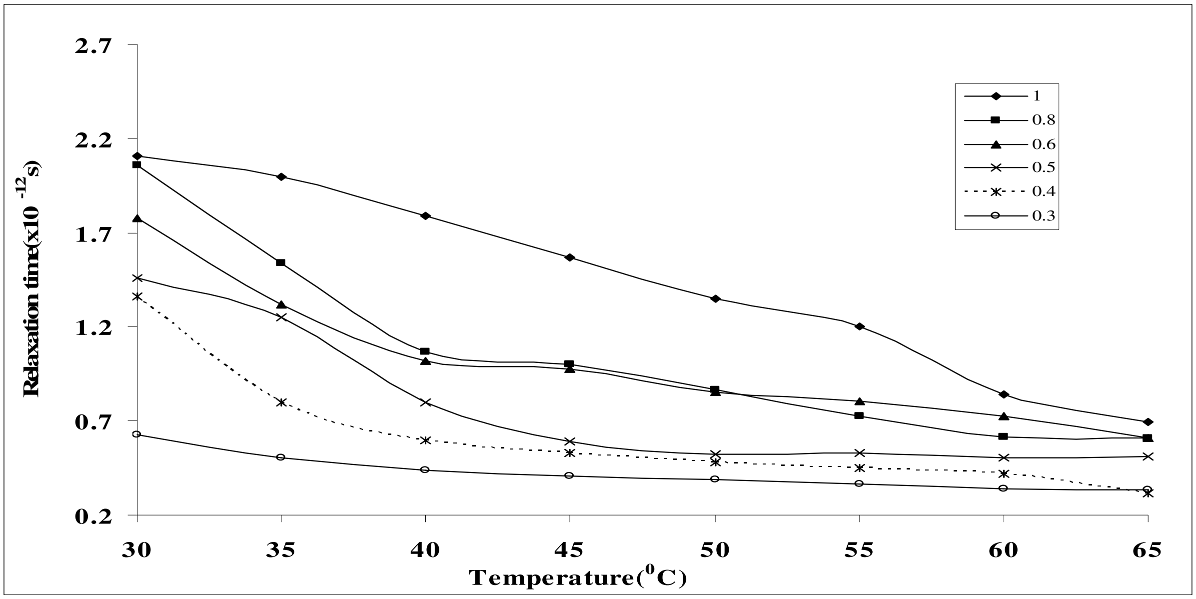

Fig.-9: Variation of relaxation time (x10^{-12}s)with temperature at different concentration of PVA

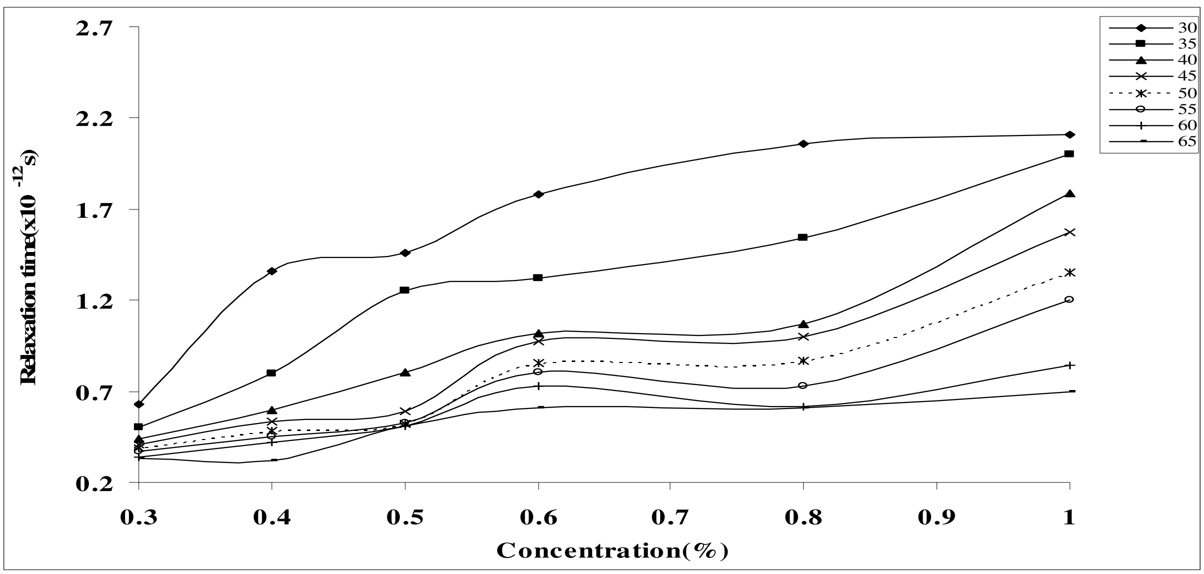

Fig.-10: Variation of relaxation time (x10^{-12}s) with concentration at different temperature of PVA

CONCLUSION

The molecular interactions present in aqueous PEG solutions have been investigated by viscosity, density, and ultrasonic velocity studies. From above study, it is concluded that there is an association between polyvinyl alcohol and water because of interaction between solvent and solute may be responsible for the increase in ultrasonic velocity, and in turns affects other parameters. It may be because of polymer molecules come close to the solvent molecules leaving sufficient space around them. The results also indicate the existence of positive interactions between polymer and water.

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