International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 2 (2017)


# A Study on Molecular Interaction and Excess Parameter Analysis of Polyethylene Glycol

**R.Padmanaban, K.Venkatramanan*, B.Sathish Kumar and M.Rashmi**

*Department of Physics, Sri Chandrasekharendra Saraswathi Viswa Mahavidyalaya, Enathur, Kanchipuram, India – 631561*

**E-Mail : kv.scsvmv@gmail.com*

## Abstract

The study of molecular interaction in binary liquid mixtures plays a vital role in the development of molecular sciences. A large number of studies have been made on the intermolecular interaction in liquid system by various methods like Ultrasonic, nuclear magnetic resonance, ultraviolet, dielectric constant, Infrared and Raman effect. In recent years, ultrasonic method has become a potential tool in providing information regarding the physico-chemical properties of liquid system [1-3]. The present investigation is related to analyse the molecular interaction (like adiabatic compressibility, intermolecular free length, free volume, etc.) and excess molecular properties of binary liquid mixtures of PEG 200 with water and benzene.

**Keywords :** Excess molecular properties, Polyethylene glycol, Molecular Interaction, Ultrasonic velocity

## INTRODUCTION

The ultrasonic technique, due to their simplicity and accuracy is being most widely used in the study of liquid state, the most complicated among the three states of matter [4]. 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 helps in understanding the nature of liquid state [5]. PEG is used in many industries such as a releasing agent for foam rubber, latex rubber in rubber industries, as a softener in antistatic agent, scouring agent, sizing agent, dying auxiliary, etc., in textile industries as well as in metal, wood paper, resin, paint and as a basic substance for the production of cream and hydrogels in cosmetic industries. PEG is a polymer composed of repeating subunit of ethylene oxide. Acoustical properties of polymer solutions have shown that ultrasonic velocity and its derived parameters provide much information on molecular interactions, which are of utmost importance for processes involving polymer production and their uses [6]. Therefore, the present investigation is carried out to study the molecular interactions in binary liquid mixtures of Polyethylene glycol 200 with water and

benzene for various compositions [0/50,10/40,20/30,25/25,30/20,40/10 and 50/0] at 303K.Using the measured values of density (ρ), relative viscosity (η), ultrasonic velocity (U) and refractive index, the thermodynamic parameters and their excess values can be computed.

## EXPERIMENTAL DETAILS

In the present investigation, liquid polyethylene glycol of molecular weight approximately 200 is used. The solutions were prepared by adding known volume of polyethylene glycol to fixed volume of water and benzene and stirring under reflex, until a clear solution was obtained. The composition range studied in the solution is 0/50,10/40,20/30,25/25,30/20,40/10 and 50/0. The ultrasonic velocities (U) of the above liquids and their mixtures were measured using multi frequency ultrasonic interferometer at a frequency of 2MHz (Mittal Enterprises Model F-81). The accuracy in the measurement of ultrasonic velocity of was within ± 0.01 m/s accuracy. The relative viscosity of the polymer solutions is studied at 303K for above concentrations using Brookfield viscometer [accuracy ±0.01 cP]. The densities at different composition were measured using 10ml specific gravity bottle and single pan macro balance. The uncertainty in density measurements was found to be about 0.01 $kg/m^3$. The temperature of viscometer, interferometer and refractometer are maintained at 303K by circulating water from a thermostat with a thermal stability of ± 0.05K.

## RESULTS AND DISCUSSION

The present work deals with the study of molecular interaction in binary liquid mixtures of PEG 200 in water and benzene for various compositions [0/50, 10/40,20/30,25/25,30/20,40/10 and 50/0] at 303K. Density (ρ), relative viscosity (η) and ultrasonic velocity (U) values are estimated for PEG 200 in water and benzene at 303K and the results are shown in Table 1. It is clear that for both the systems, the density and relative viscosity values show linear variation with composition i.e., the value is minimum for lower composition and maximum for higher composition. But the ultrasonic velocity values vary linearly in benzene due to molecular association and non-linearly in water due to molecular dissociation, with various compositions and it is vice-versa in the case of refractive index. The increase or decrease in these parameters with various compositions shows the existence of strong interactions between the components of molecules in the binary mixtures. This indicates the Dipole-dipole interaction or hydrogen bonded complex formation between unlike molecules [7].

**Table 1 Density, Relative Viscosity and Ultrasonic Velocity Values For PEG 200 in Water and Benzene at 303k**

| Compound Name | Composition range (ml) | Density ($kg/m^3$) | Relative Viscosity (cP) | Ultrasonic Viscosity (m/s) |
|---|---|---|---|---|
| PEG 200 + Water | 0/50 | 0995.9 | 01.02 | 1503.461 |
| | 10/40 | 1028.8 | 01.72 | 1602.299 |
| | 20/25 | 1062.2 | 03.84 | 1662.706 |
| | 25/25 | 1076.2 | 05.90 | 1701.656 |
| | 30/20 | 1091.6 | 09.30 | 1704.788 |
| | 40/10 | 1109.7 | 22.50 | 1657.499 |
| | 50/0 | 1116.2 | 36.60 | 1567.719 |
| PEG 200 + Benzene | 0/50 | 0866.3 | 00.86 | 1266.082 |
| | 10/40 | 0910.4 | 01.05 | 1284.074 |
| | 20/25 | 0972.1 | 02.83 | 1346.618 |
| | 25/25 | 1001.1 | 04.58 | 1386.949 |
| | 30/20 | 1030.2 | 08.04 | 1430.875 |
| | 40/10 | 1080.9 | 18.90 | 1512.052 |
| | 50/0 | 1116.2 | 36.60 | 1567.719 |

From the observed values of density, ultrasonic velocity and viscosity the molecular interaction parameters like adiabatic compressibility, intermolecular free length, free volume, internal pressure and their excess values have been computed for various compositions [0/50,10/40,20/30,25/25,30/20,40/10 and 50/0] at 303K.

In this study the adiabatic compressibility for PEG 200 in water and benzene decreases as the concentration increases [Fig. 1] that the molecules are closely packed in the solution. Its value is high at lower composition and minimum for higher composition range. The adiabatic compressibility shows an inverse behavior as compared to ultrasonic velocity in both the cases. This suggests that there is a significant interaction between solute and solvent molecules indicating the formation of complexes. The intermolecular free length decreases with the increase in composition for both the system [Fig. 2]. In general, for PEG 200 in water and benzene, at lower concentration range the molecules exhibit weak interaction due to

dominant repulsive force and at higher concentration there is a specific interaction among the molecules [8].

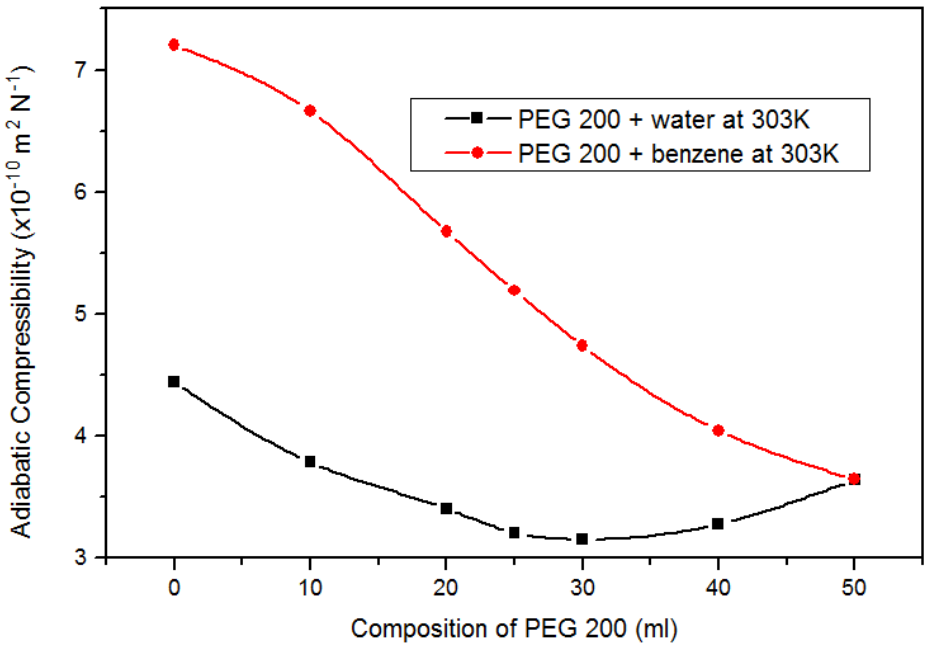


**Fig. 1 Variation of Adiabatic compressibility against Composition of PEG 200**

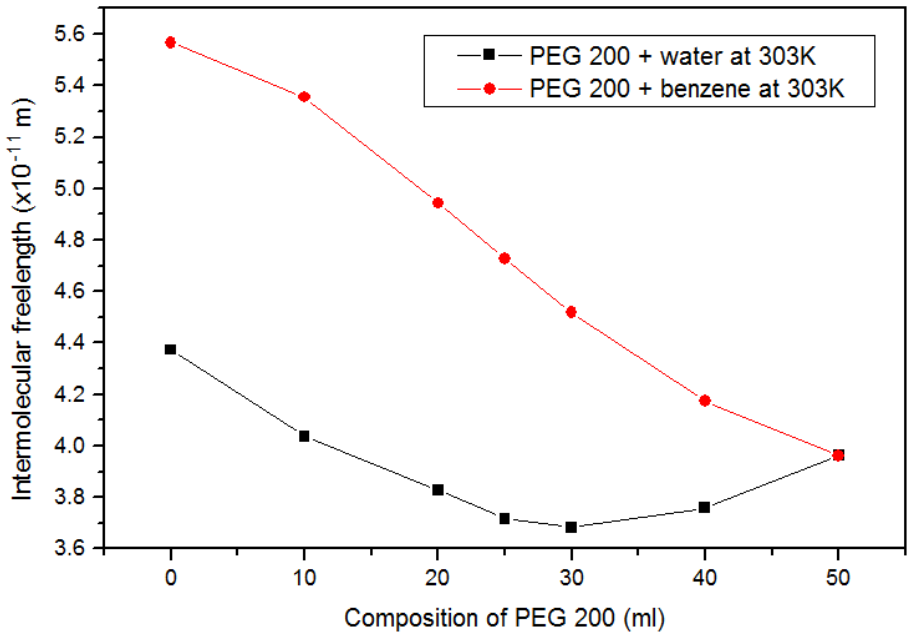


**Fig. 2 Variation of Intermolecular free length against Composition of PEG 200**

Due to greater forces of interaction between solute and solvent molecules, hydrogen bond formation occur which results in a decrease in free length of the mixture. As a result of this the ultrasonic velocity increases. The free volume directly depends on ultrasonic velocity and inversely on viscosity [Fig. 3 & 4]. Therefore, viscosity rather than velocity determines the free volume and the free volume reduces when the internal pressure increases. In the present study, free volume for PEG 200 in water gradually decreases. But in benzene, it is observed that PEG 200 decreases very sharply. Internal pressure is a measure of the resultant attractive and repulsive forces between the interacting components in the mixture. The variation of internal pressure [Fig. 3 & 4] with composition of PEG 200 in water and benzene is observed as non-linear. The internal pressure is minimum at lower composition with a value of (2.6563 x $10^9$ atm & 0.4348 x $10^9$ atm for PEG 200 in water and benzene respectively) and maximum with a value of 3.2137 x $10^9$ atm (30/20 composition) & 1.4035 x $10^9$ atm (40/10 composition) for PEG 200 in water and benzene respectively. Thus the internal pressure shows reverse trend to free volume.

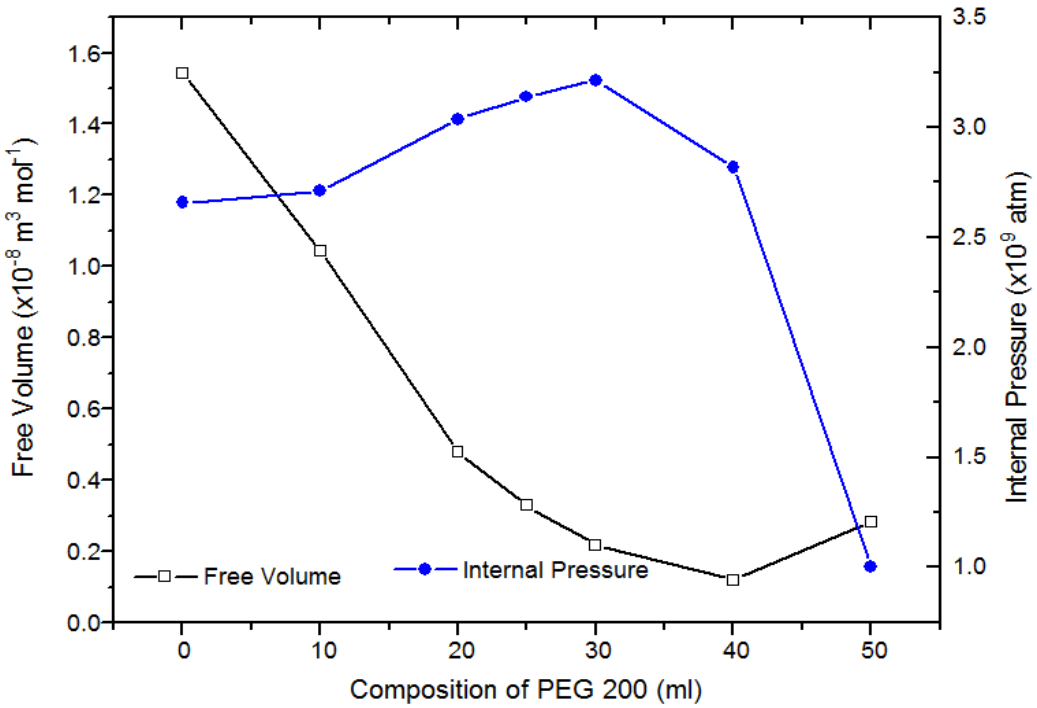


**Fig. 3 Variation of Free volume and Internal Pressure against Composition of PEG 200 in water**

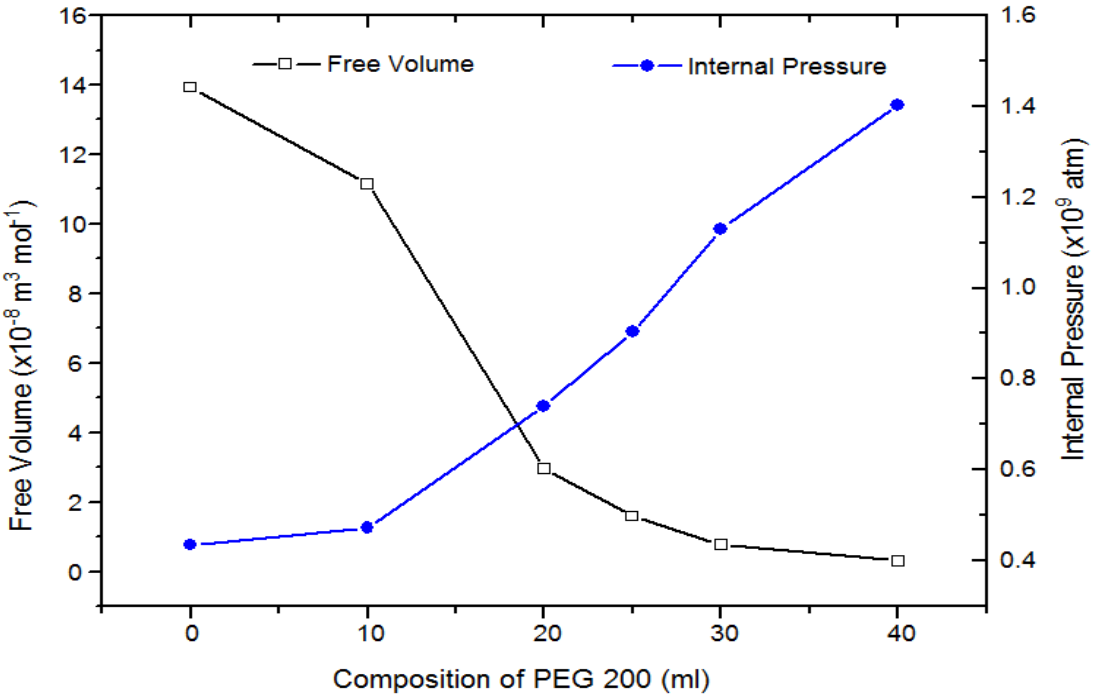


**Fig. 4 Variation of Free volume and Internal Pressure against Composition of PEG 200 in benzene**

From the experimental values of molecular interaction parameters, their excess values are calculated for various composition [0/50, 10/40, 20/30, 25/25, 30/20, 40/10 and 50/0] at 303K.

The excess molecular interaction parameters are calculated using the formula given below.

Excess Adiabatic compressibility, $\beta^E_{ad} = \beta_{ad} - (\beta_{ad1} X_1 + \beta_{ad2} X_2)$
Excess Intermolecular Free Length, $L_f^E = L_f - (L_{f1} X_1 + L_{f2} X_2)$
Excess Free Volume, $V_f^E = V_f - (V_{f1} X_1 + V_{f2} X_2)$
Excess Internal Pressure, $\pi^E = \pi - (\pi_1 X_1 + \pi_2 X_2)$

The excess values of adiabatic compressibility ($\beta^E_{ad}$), intermolecular free length ($L_f^E$) and free volume ($V_f^E$) are found negative in the systems of PEG 200 + water and PEG 200 + benzene for various compositions [0/50, 10/40, 20/30, 25/25, 30/20, 40/10 and 50/0] at 303K [Fig. 5-7]. This indicates the presence of strong interaction between the components of the mixtures [9].

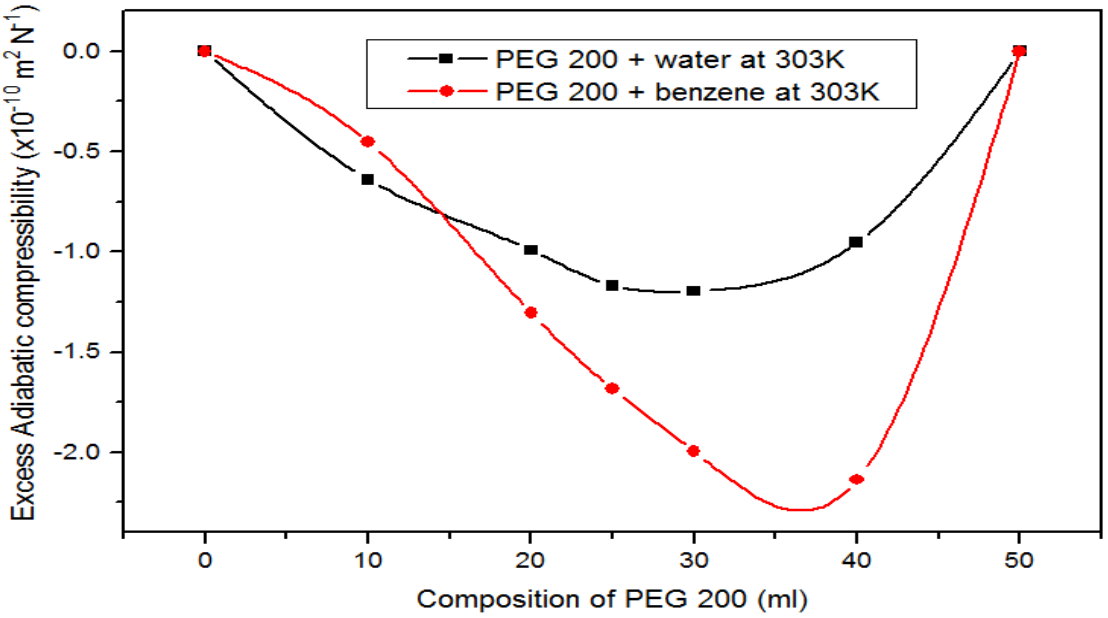


**Fig. 5 Variation of Excess adiabatic compressibility against Composition of PEG 200**

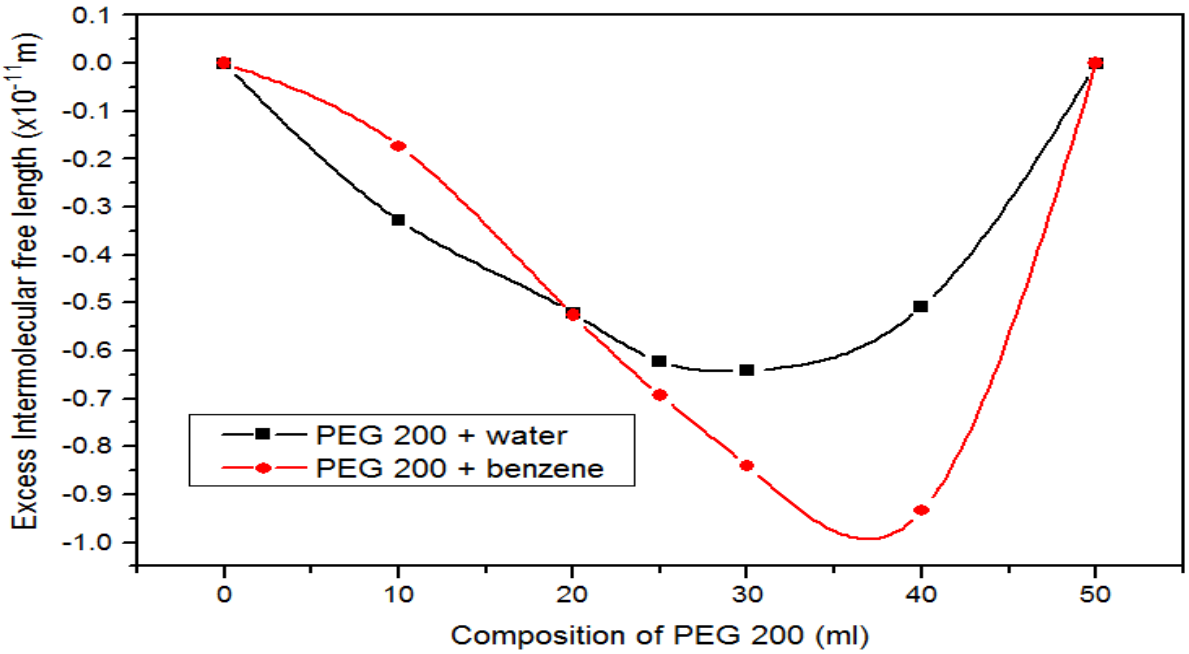


**Fig. 6 Variation of Excess intermolecular free length against Composition of PEG 200**

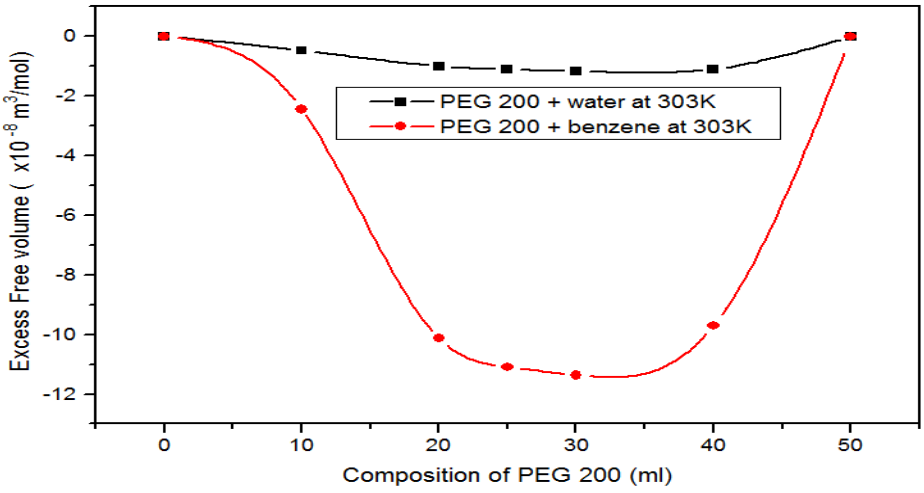


**Fig. 7 Variation of Excess Free volume against Composition of PEG 200**

The Internal pressure ($\pi^E$) is found positive in the systems of PEG 200 + water and PEG 200 + benzene for various composition [0/50,10/40,20/30,25/25,30/20,40/10 and 50/0] at 303K [Fig. 8]. This indicates the presence of weak interaction between the components of the molecules [9].

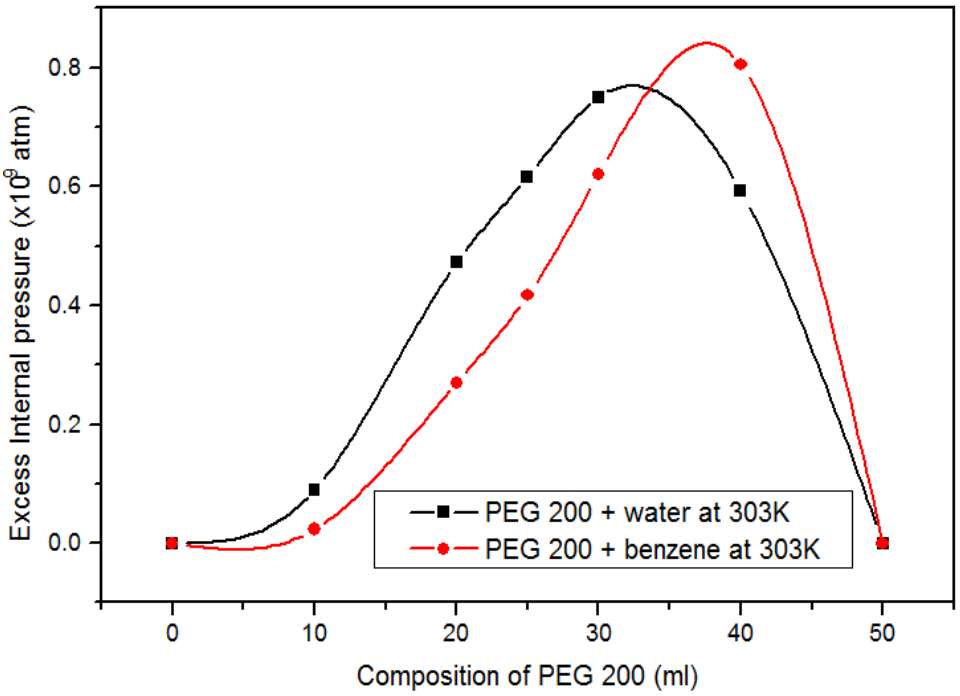


**Fig. 8 Variation of Excess Internal pressure against Composition of PEG 200**

## CONCLUSION

In the present investigation, density, viscosity and ultrasonic velocity are studied for the binary liquid mixtures of PEG 200 for various concentrations at 303K. From these experimental values, various molecular interaction parameters and excess parameters are determined. The excess values of adiabatic compressibility, intermolecular free length and free volume are found negative in both the systems and it shows the existence of strong interactions between the component of molecules whereas the excess values of internal pressure are found to be positive in both systems indicating the weak intermolecular interaction between the component molecules.

## REFERENCES

[1] Venkatramanan, K. et al. Thermodynamic Studies on Biocompatible Polymer, *Advanced Science Letters*, 22, 11, (2016), pp. 3948-3950.

[2] Padmanaban, R. and Venkatramanan, K. Miscibility studies of Polyethylene Glycol with Polystyrene in Toluene by Various Physical and Advanced Techniques, *Journal of Physics : Conference Series*, 759, (2016), pp. 012017.

[3] Venkatramanan, K. et al. Acoustic, Thermal and Molecular Interactions of Polyethylene Glycol (2000, 3000, 6000), *Physics Procedia*,70, (2015), pp. 1052-1056.

[4] Grace Sahaya Sheba, S. and Omegala Priakumari, R. Ultrasonic Investigation of Molecular Interaction in Binary Liquid Mixture of Polyethylene Glycol with Ethanol, *International Journal of Chemical, Molecular, Nuclear, Materials and Metallurgical Engineering*, 8, 2, (2014), pp. 156-160.

[5] Neeraja, P. and Ubagaramary, D. Ultrasonic studies on molecular interactions in Binary mixtures of IBMK with Carbonyl Molecules, *International Refereed Journal of Engineering and Science*, 1, 4, (2012), pp. 54-77.

[6] Syal, V.K. et al. Ultrasonic velocity, viscosity and density studies of poly (ethylene glycols) (PEG - 8,000, PEG - 20,000) in acetonitrile (AN) and water (H2O) mixtures at 25° C, *Journal of Pure and Applied Ultrasonics*, 27, (2005), pp.61-69.

[7] Ravichandran, S. Acoustic and thermodynamic properties of cholesterol in ethanol and1-propanol solution in different concentration at 303K, *Research Journal of Chemical Sciences*, 1, 8, (2011), pp. 12-17.

[8] Asghar, J. et al. Thermodynamic studies of molecular interactions in ternary liquid mixtures at various temperatures, *Rasaya. J. Chem.*, 3, 4, (2010), pp. 697-704.

[9] Fort, R. J. et al. Adiabatic compressibilities of binary liquid mixtures, *Trans. Faraday Society*, 61, (1965), pp. 2102-2111.