



## A study on solutions of poly (vinylpyrrolidone) in binary mixtures of DMSO+H<sub>2</sub>O at different temperatures by ultrasonic velocity measurements

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**Abstract** – The ultrasonic velocities and densities of solutions of poly (vinylpyrrolidone) *i.e.* (PVP) (Mol. wt  $\approx$  40,000) have been measured in water and its binary mixtures with dimethylsulphoxide (DMSO) containing DMSO at 25 mol % intervals at 25°C, 35°C and 45°C. From velocity and density values, various acoustical parameters such as acoustical impedance ( $Z$ ), adiabatic compressibility ( $\beta$ ), intermolecular free length ( $L_f$ ), relative association ( $R_A$ ), molar sound velocity ( $R$ ), Wada's constant ( $W$ ), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\kappa}$ ) have been evaluated. All these parameters have been discussed separately in terms of polymer-polymer and polymer-solvent interactions as a function of solvent composition and temperature.

**Keywords** – Ultrasonic velocity, density, poly(vinylpyrrolidone), dimethylsulphoxide (DMSO)

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### 1. Introduction

PVP is a water-soluble polymer and has large number of applications in industry, medicine and research *etc* [1,2]. Because of its diverse applications, considerable attention has been paid by the researchers in the study of interactions between macromolecules, solvent system and salts through various techniques, namely, ultrasonic velocity and viscosity *etc*. Some studies have been performed on polymer solutions by several investigators using ultrasonic velocity measurements in recent years [3,4] in order to understand polymer-solvent and polymer-polymer interactions and also structure of polymers. Therefore, in this communication, ultrasonic velocity and density measurements of solutions of poly (vinylpyrrolidone) in binary aqueous mixtures of dimethylsulphoxide have been reported over whole solvent composition range at 25°C, 35°C and 45°C. The various acoustical parameters thus derived from above data, have been discussed in terms of polymer-polymer and polymer-solvent interactions.

### 2. Experimental

The solvents, water and dimethyl sulfoxide (DMSO) have been

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purified as reported earlier [5]. Polymer poly (vinylpyrrolidone) *i.e.* (C<sub>6</sub>H<sub>9</sub>NO)<sub>n</sub> (Extrapure, Sisco Research Laboratories Pvt. Ltd. Bombay) has been used as such, after drying for few hours. The solutions were prepared by adding a known weight of polymer to a fixed volume of solvent/solvent mixture and then stirring until a clear solution was obtained. The low concentration range (0% to 0.6%) has been studied in the solutions because of its high viscous nature.

Ultrasonic velocity ( $U$ ) was measured at 1MHz using interferometer supplied by Mittal Enterprises, New Delhi which is a direct and simple device for measuring sound velocity in liquids.

A detailed procedure for the measurement of ultrasonic velocity and density ( $\rho$ ) is described elsewhere [6]. The accuracy of both density and ultrasonic velocity measurements was estimated to be  $\pm 0.002\%$  and  $\pm 0.05\%$ , respectively.

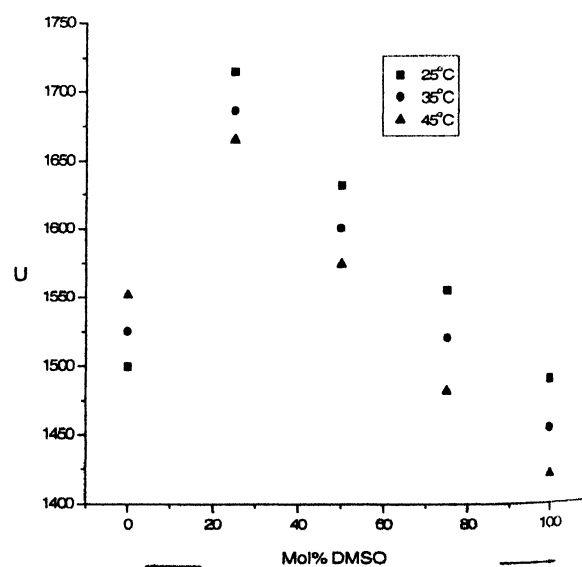
### 3. Results and discussion

The various measured and derived acoustical parameters of poly (vinylpyrrolidone) presented in Tables 1-5, have been calculated using the equations given in the literature [7-10]. The ultrasonic

**Table 1.** Wt%age (v/v), ultrasonic velocity ( $U$ ), density ( $\rho$ ), adiabatic compressibility ( $\beta$ ), specific acoustic impedance ( $Z$ ), Inter molecular free length ( $L_f$ ), relative association ( $R_A$ ), molar sound velocity ( $R$ ), Wada's constant ( $W$ ), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\Delta}$ ) of PVP in 100 % H<sub>2</sub>O at different temperatures.

| Temperature | v/v-% | $\rho \times 10^3$<br>Kg m <sup>-3</sup> | $U$<br>m s <sup>-1</sup> | $\beta \times 10^{10}$<br>m <sup>2</sup> N <sup>-1</sup> | $Z \times 10^6$<br>Kg m <sup>2</sup> s <sup>-1</sup> | $L_f \times 10^{11}$ m | $R \times 10^2$<br>m <sup>10/3</sup> s <sup>-1/3</sup> | $W \times 10^{11/7}$<br>m <sup>19/7</sup> N <sup>1/7</sup> | $S_n \times 10^2$ | $\phi_{\Delta} \times 10$<br>m <sup>3</sup> s <sup>2</sup> kg |
|-------------|-------|--|--------------------------|--|--|------------------------|--|--|-------------------|---|
| 25°C        | 0.0   | 0.9970                                   | 1500.0                   | 4.4578   | 1.4955   | 4.3426                 | 20.66  | 14.58  | ---               | 178.85  |
|             | 0.1   | 0.9971                                   | 1502.6                   | 4.4420   | 1.4980   | 4.3349                 | 20.67  | 14.59  | 78.68             | 178.03  |
|             | 0.2   | 0.9973                                   | 1503.4                   | 4.4363   | 1.4993   | 4.3322                 | 20.67  | 14.59  | 53.48             | 177.82  |
|             | 0.3   | 0.9975                                   | 1504.4                   | 4.4296   | 1.5006   | 4.3289                 | 20.67  | 14.59  | 46.72             | 177.52  |
|             | 0.4   | 0.9977                                   | 1505.6                   | 4.4216   | 1.5021   | 4.3250                 | 20.67  | 14.59  | 44.94             | 177.15  |
|             | 0.5   | 0.9979                                   | 1506.3                   | 4.4166   | 1.5031   | 4.3225                 | 20.67  | 14.59  | 40.87             | 176.93  |
|             | 0.6   | 0.9981                                   | 1507.2                   | 4.4105   | 1.5043   | 4.3195                 | 20.67  | 14.59  | 39.06             | 176.66  |
| 35 °C       | 0.0   | 0.9941                                   | 1525.4                   | 4.3232   | 1.5161   | 4.3545                 | 20.84  | 14.69  | ---               | 173.95  |
|             | 0.1   | 0.9942                                   | 1527.3                   | 4.3120   | 1.5184   | 4.3489                 | 20.85  | 14.69  | 57.51             | 173.36  |
|             | 0.2   | 0.9944                                   | 1529.4                   | 4.2993   | 1.5208   | 4.3425                 | 20.85  | 14.69  | 61.30             | 172.81  |
|             | 0.3   | 0.9946                                   | 1530.8                   | 4.2906   | 1.5225   | 4.3381                 | 20.85  | 14.69  | 55.68             | 172.44  |
|             | 0.4   | 0.9948                                   | 1533.2                   | 4.2763   | 1.5252   | 4.3309                 | 20.86  | 14.70  | 60.03             | 171.87  |
|             | 0.5   | 0.9950                                   | 1535.0                   | 4.2654   | 1.5273   | 4.3254                 | 20.86  | 14.71  | 59.12             | 171.35  |
|             | 0.6   | 0.9953                                   | 1537.2                   | 4.2519   | 1.5300   | 4.3185                 | 20.87  | 14.71  | 60.72             | 170.78  |
| 45°C        | 0.0   | 0.9902                                   | 1551.7                   | 4.1943   | 1.5365   | 4.3660                 | 21.05  | 14.81  | ---               | 169.4   |
|             | 0.1   | 0.9904                                   | 1553.4                   | 4.1843   | 1.5385   | 4.3607                 | 21.05  | 14.81  | 52.93             | 168.88  |
|             | 0.2   | 0.9905                                   | 1554.8                   | 4.1763   | 1.5400   | 4.3566                 | 21.05  | 14.82  | 47.58             | 168.56  |
|             | 0.3   | 0.9907                                   | 1556.4                   | 4.1669   | 1.5419   | 4.3517                 | 21.05  | 14.82  | 48.25             | 168.14  |
|             | 0.4   | 0.9908                                   | 1558.0                   | 4.1579   | 1.5437   | 4.3470                 | 21.06  | 14.82  | 48.02             | 167.76  |
|             | 0.5   | 0.9910                                   | 1559.6                   | 4.1486   | 1.5456   | 4.3421                 | 21.06  | 14.82  | 48.18             | 167.35  |
|             | 0.6   | 0.9912                                   | 1561.0                   | 4.1403   | 1.5473   | 4.3378                 | 21.06  | 14.83  | 47.39             | 166.98  |

velocity varies linearly with the increase in concentration of polymer in water, DMSO and all the studied mixtures. However, the velocity change is no more linear with the change in solvent composition as DMSO is added to water. In pure solvents, the velocity value shows a maximum at about 20-30 mol % and nearly 25 mol % DMSO Figure 1, which is in agreement as reported earlier [5]. Such a maximum has also been observed in other aquo-organic mixtures like methanol + water and ethanol + water [11]. This nonlinear behaviour of velocity with solvent composition has been attributed to the existence of solvent – solvent interactions, which are maximized nearer to 25 mol % of DMSO, which has been further supported by spectroscopic and other studies [11]. The purpose of this study is to observe the behaviour of velocity in these binary aqueous solvent mixtures after adding polymer as solute. It is clear from the Tables (1-5) that the magnitude of velocity increases with the addition of polymer but the velocity behavior remains the same as in the pure solvent mixtures. This clearly indicates that the solute-solvent interactions though present, hardly break the solvent-solvent interactions already present in the binary solvent mixtures. The same is true for maltose and fructose carbohydrates



**Figure 1.** Plot of ultrasonic velocity ( $U$ ) versus mol% DMSO in DMSO + H<sub>2</sub>O solvent system of PVP at different temperatures.

Table 2. Wt% age (v/v), ultrasonic velocity (U), density ( $\rho$ ), adiabatic compressibility ( $\beta$ ), specific acoustic impedance (Z), Inter molecular free length ( $L_f$ ), relative association ( $R_A$ ), molar sound velocity (R), Wada's constant (W), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\lambda}$ ) of PVP in 25 mol % DMSO at different temperatures

| Temperature | v/v% | $\rho \times 10^{-3}$<br>Kg m <sup>-3</sup> | U      | $\beta \times 10^{10}$<br>m <sup>2</sup> N <sup>-1</sup> | $Z \times 10^{-6}$<br>Kg m <sup>-2</sup> s <sup>-1</sup> | $L_f \times 10^{11}$ m | $R \times 10^2$ | $W \times 10^{11/7}$<br>m <sup>19/7</sup> N <sup>1/7</sup> | $S \times 10^2$ | $\phi_{\lambda} \times 10^{10}$<br>m <sup>2</sup> s <sup>2</sup> kg <sup>-1</sup> |
|-------------|------|---|--------|--|--|------------------------|-----------------|--|-----------------|---|
| 35 °C       | 0.0  | 1.0808                                      | 1714.9 | 3.1461   | 1.8534   | 3.6481                 | 24.68           | 17.51  | ---             | 116.44  |
|             | 0.1  | 1.0816                                      | 1716.2 | 3.1390   | 1.8562   | 3.6440                 | 24.67           | 17.50  | 40.46           | 115.97  |
|             | 0.2  | 1.0818                                      | 1717.0 | 3.1384   | 1.8574   | 3.6437                 | 24.67           | 17.50  | 30.17           | 115.87  |
|             | 0.3  | 1.0821                                      | 1718.6 | 3.1288   | 1.8597   | 3.6382                 | 24.67           | 17.50  | 32.79           | 115.59  |
|             | 0.4  | 1.0824                                      | 1719.6 | 3.1243   | 1.8613   | 3.6356                 | 24.66           | 17.50  | 30.96           | 115.39  |
|             | 0.5  | 1.0827                                      | 1720.5 | 3.1202   | 1.8628   | 3.6332                 | 24.66           | 17.50  | 29.40           | 115.22  |
|             | 0.6  | 1.0829                                      | 1721.3 | 3.1167   | 1.8640   | 3.6311                 | 24.66           | 17.50  | 27.78           | 115.07  |
| 35 °C       | 0.0  | 1.0740                                      | 1686.4 | 3.2740   | 1.8111   | 3.7895                 | 24.70           | 17.52  | ---             | 121.94  |
|             | 0.1  | 1.0741                                      | 1688.3 | 3.2663   | 1.8134   | 3.7850                 | 24.71           | 17.52  | 42.16           | 121.56  |
|             | 0.2  | 1.0742                                      | 1690.3 | 3.2583   | 1.8157   | 3.7804                 | 24.72           | 17.53  | 42.94           | 121.25  |
|             | 0.3  | 1.0743                                      | 1692.0 | 3.2514   | 1.8177   | 3.7764                 | 24.72           | 17.53  | 41.17           | 121.06  |
|             | 0.4  | 1.0745                                      | 1694.1 | 3.2428   | 1.8203   | 3.7714                 | 24.73           | 17.53  | 42.58           | 120.64  |
|             | 0.5  | 1.0746                                      | 1695.5 | 3.2371   | 1.8220   | 3.7681                 | 24.73           | 17.54  | 40.25           | 120.42  |
|             | 0.6  | 1.0747                                      | 1697.3 | 3.2299   | 1.8241   | 3.7639                 | 24.74           | 17.54  | 40.05           | 120.15  |
| 45 °C       | 0.0  | 1.0656                                      | 1665.2 | 3.3843   | 1.7744   | 3.9217                 | 24.79           | 17.57  | ---             | 127.04  |
|             | 0.1  | 1.0657                                      | 1665.9 | 3.3812   | 1.7753   | 3.9199                 | 24.79           | 17.57  | 15.33           | 126.87  |
|             | 0.2  | 1.0658                                      | 1666.5 | 3.3784   | 1.7762   | 3.9183                 | 24.79           | 17.57  | 14.15           | 126.76  |
|             | 0.3  | 1.0659                                      | 1667.1 | 3.3756   | 1.7769   | 3.9167                 | 24.79           | 17.57  | 14.53           | 126.65  |
|             | 0.4  | 1.0661                                      | 1667.8 | 3.3722   | 1.7780   | 3.9147                 | 24.79           | 17.57  | 14.59           | 126.50  |
|             | 0.5  | 1.0662                                      | 1668.4 | 3.3695   | 1.7788   | 3.9132                 | 24.79           | 17.57  | 14.25           | 126.37  |
|             | 0.6  | 1.0663                                      | 1669.0 | 3.3667   | 1.7796   | 3.9115                 | 24.79           | 17.57  | 14.48           | 126.26  |

taken as solutes in binary aqueous DMSO mixtures at all concentrations [5]. The variation of velocity with concentration is similar at all temperatures.

The adiabatic compressibility ( $\beta$ ) values of polymer solution also vary nonlinearly with the change in solvent composition giving a minimum at about same composition range i.e. around 25 mol % DMSO indicating that solvent-solvent interactions are maximum in the same region of almost 25 mol % DMSO [5]. In Ref. [5], the ultrasonic velocity shows maximum at 30 mol% of DMSO, (given in Figure 1 as well as Table 1). The  $\beta$ -values decrease with increase in concentration of polymer. The decrease in  $\beta$ -values is due to the influence of solute on the surrounding solvent molecules leading to increase in internal pressure and thus the solution becomes harder to compress. The increase in internal pressure with the increase of concentration of polymer has been obtained in this case and this supports the above argument. Similar observations for the decrease of  $\beta$  has been reported in the literature of Shah and Parsania[4] for poly (4,4'-cyclohexylidene-2,2'-dimethyldiphenylene/diphenylene-3,3'-benzophenone

disulphonates) in chlorinated and aprotic solvents. Since polymer chains assume a variety of conformational changes under different experimental conditions like concentration, temperature, dielectric constant of the medium etc., the polymer may assume a coiled configuration in concentrated solutions and unfold to a greater extent on dilution in polar solvents which results in increase of viscosity. Since flexible polymers are more compressible due to chain like structure which is further supported by the decrease in isentropic compressibility (coiling up of polymer chain) with increasing concentration[4]. Such reduction in compressibility has been found in solutions of cellulose derivatives and polymer solutions of polystyrene in toluene[12]. With the increase in temperature, since adiabatic compressibilities increase, it clearly indicates temperature dependence of  $\beta$ . The value of intermolecular free length  $L_f$  shows a decreasing trend, which is in agreement with the observation made by Syal and coworkers[13] in case of ultrasonic studies of alkali bromides in DMSO + dioxane solvent system at 25°C. With increase in temperature, the magnitude of  $L_f$  increases, and is in good agreement with the theoretical

**Table 3.** Wt% age ( $v/v\%$ ), ultrasonic velocity ( $U$ ), density ( $\rho$ ), adiabatic compressibility ( $\beta$ ), specific acoustic impedance ( $Z$ ), Inter molecular free length ( $L_f$ ), relative association ( $R_s$ ), molar sound velocity ( $R$ ), Wada's constant ( $W$ ), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\lambda}$ ) of PVP in 50 mol % DMSO at different temperatures

| Temperature | $v/v\%$ | $\rho \times 10^{-3}$<br>Kg m <sup>-3</sup> | $U$<br>m s <sup>-1</sup> | $\beta \times 10^{10}$<br>m <sup>2</sup> N <sup>-1</sup> | $Z \times 10^{-6}$<br>Kg m <sup>-2</sup> s <sup>-1</sup> | $L_f \times 10^{11}$ m | $R \times 10^2$<br>m <sup>10/3</sup> s <sup>-1/3</sup> | $W \times 10^{11/7}$<br>m <sup>19/7</sup> N <sup>1/7</sup> | $S_n \times 10^{-2}$ | $\phi_{\lambda} \times 10$<br>m <sup>3</sup> s <sup>-2</sup> Kg <sup>-1</sup> |
|-------------|---------|---|--------------------------|--|--|------------------------|--|--|----------------------|---|
| 25°C        | 0.0     | 1.0986                                      | 1632.0                   | 3.4176   | 1.7929   | 3.8023                 | 31.35  | 22.35  | ---                  | 124.43  |
|             | 0.1     | 1.0988                                      | 1632.5                   | 3.4149   | 1.7938   | 3.8009                 | 31.35  | 22.34  | 10.78                | 124.28  |
|             | 0.2     | 1.0989                                      | 1634.0                   | 3.4083   | 1.7956   | 3.7972                 | 31.36  | 22.35  | 18.56                | 124.02  |
|             | 0.3     | 1.0991                                      | 1635.4                   | 3.4018   | 1.7975   | 3.7936                 | 31.36  | 22.35  | 21.00                | 123.75  |
|             | 0.4     | 1.0993                                      | 1636.4                   | 3.3971   | 1.7989   | 3.7909                 | 31.36  | 22.35  | 20.42                | 123.55  |
|             | 0.5     | 1.0994                                      | 1638.0                   | 3.3901   | 1.8008   | 3.7870                 | 31.37  | 22.35  | 21.89                | 123.20  |
|             | 0.6     | 1.0995                                      | 1638.3                   | 3.3886   | 1.8013   | 3.7864                 | 31.37  | 22.35  | 19.22                | 123.23  |
| 35 °C       | 0.0     | 1.0894                                      | 1600.5                   | 3.5834   | 1.7436   | 3.9645                 | 31.42  | 22.38  | ---                  | 131.57  |
|             | 0.1     | 1.0895                                      | 1601.7                   | 3.5778   | 1.7451   | 3.9614                 | 31.42  | 22.38  | 21.34                | 131.29  |
|             | 0.2     | 1.0896                                      | 1602.9                   | 3.5721   | 1.7465   | 3.9582                 | 31.43  | 22.38  | 21.51                | 131.05  |
|             | 0.3     | 1.0897                                      | 1604.2                   | 3.5660   | 1.7481   | 3.9548                 | 31.43  | 22.39  | 22.06                | 130.87  |
|             | 0.4     | 1.0898                                      | 1605.0                   | 3.5621   | 1.7491   | 3.9527                 | 31.43  | 22.39  | 20.23                | 130.69  |
|             | 0.5     | 1.0899                                      | 1606.6                   | 3.5547   | 1.7510   | 3.9486                 | 31.44  | 22.39  | 21.78                | 130.40  |
|             | 0.6     | 1.0990                                      | 1607.2                   | 3.5226   | 1.7663   | 3.9307                 | 31.44  | 22.39  | 21.34                | 128.67  |
| 45°C        | 0.0     | 1.0801                                      | 1574.6                   | 3.7342   | 1.7007   | 4.1195                 | 31.52  | 22.44  | ---                  | 138.29  |
|             | 0.1     | 1.0802                                      | 1575.1                   | 3.7315   | 1.7014   | 4.1180                 | 31.52  | 22.44  | 19.97                | 138.11  |
|             | 0.2     | 1.0803                                      | 1575.6                   | 3.7287   | 1.7021   | 4.1164                 | 31.52  | 22.44  | 19.95                | 138.01  |
|             | 0.3     | 1.0804                                      | 1576.2                   | 3.7255   | 1.7029   | 4.1147                 | 31.52  | 22.44  | 19.52                | 137.96  |
|             | 0.4     | 1.0805                                      | 1576.9                   | 3.7228   | 1.7036   | 4.1132                 | 31.52  | 22.44  | 17.84                | 137.79  |
|             | 0.5     | 1.0806                                      | 1577.2                   | 3.7202   | 1.7043   | 4.1117                 | 31.52  | 22.44  | 18.65                | 137.68  |
|             | 0.6     | 1.0808                                      | 1577.8                   | 3.7166   | 1.7053   | 4.1098                 | 31.52  | 22.44  | 19.12                | 137.32  |

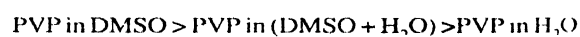
requirements and the literature data. However, the behaviour of  $\beta$  and  $L_f$  in water and various water + DMSO mixtures gives minimum for  $\beta$  and  $L_f$  nearer to 25 mol % DMSO.

The value of  $Z$  shows gradual increase with the increase of concentration of polymer in water and other mixtures. This is in agreement with the theoretical requirement because  $U$  and  $\rho$  both increase with the increase of concentration. However, the  $Z$ -values show maximum in the same region of 20-30 mol % and nearer to 25 mol % DMSO. Increase of  $Z$ , with concentration of polymer has also been reported by Sanariya and Parsania [14].

The decrease of  $\beta$ , and increase of  $U$  and  $Z$  with increasing concentrations in a particular system, is indicative of strong polymer – solvent interaction. This is further supported by non-linear increase of  $R$  and decrease of  $L_f$  with concentration [4].

It has been found that molar sound velocity ( $R$ ) and molar adiabatic compressibility represented as Wada's constant ( $W$ ) are independent of temperature, pressure and concentration, which is in accordance with the  $R$  and  $W$ -values for unassociated and weakly associated molecules [6]. However,  $R$  and  $W$ -values are found to increase as DMSO content is increased in the

solvent mixture *i.e.*,  $R$  and  $W$  values of PVP in these systems are in the following order:



which is supported by the 2:1 complex formation of H<sub>2</sub>O with DMSO mixture as given earlier [11]. Similar observations have been obtained for PEG in DMSO+H<sub>2</sub>O system by Srilalitha and coworkers [8]. Higher values of  $R$  and  $W$  in H<sub>2</sub>O + DMSO systems have been obtained as compared to the PVP in H<sub>2</sub>O, similar to that reported by Srilalitha and coworkers [8]. In the present study, H<sub>2</sub>O+DMSO solvent system may also have 2:1 complex formation and interaction between this complex and PVP may be responsible for the higher ultrasonic velocities and  $R$ -values of PVP in H<sub>2</sub>O + DMSO solvent system compared to other system *i.e.* PVP in H<sub>2</sub>O. The higher values of  $R$  in DMSO in comparison to its value in H<sub>2</sub>O may be accounted for the non-formation of hydrogen bonding in PVP-DMSO system whereas there may be molecular association by hydrogen bonding of PVP with water. This may be possible at the oxygen sites in PVP in H<sub>2</sub>O and H<sub>2</sub>O+DMSO system. Similar results have been reported by Srilalitha and coworkers [8] for PEG in DMSO+H<sub>2</sub>O solvent system. Similar temperature invariance of Rao's number and

Table 4. Wt% age (v/v), ultrasonic velocity (U), density ( $\rho$ ), adiabatic compressibility ( $\beta$ ), specific acoustic impedance (Z), Inter molecular free length ( $L_f$ ), relative association ( $R_r$ ), molar sound velocity (R), Wada's constant (W), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\lambda}$ ) of PVP in 75 mol % DMSO at different temperatures.

| Temperature | v/v% | $\rho \times 10^{-3}$<br>Kg m <sup>-3</sup> | U<br>m s <sup>-1</sup> | $\beta \times 10^{10}$<br>m <sup>2</sup> N <sup>-1</sup> | $Z \times 10^6$<br>Kg m <sup>-2</sup> s <sup>-1</sup> | $L_f \times 10^{11}$ m | $R \times 10^3$<br>m <sup>10/3</sup> s <sup>1/3</sup> | $W \times 10^{11/7}$<br>m <sup>19/7</sup> N <sup>1/7</sup> | $S_n \times 10^2$ | $\phi_{\lambda} \times 10^{10}$<br>m <sup>4</sup> s <sup>-2</sup> kg <sup>-1</sup> |
|-------------|------|---|------------------------|--|---|------------------------|---|--|-------------------|--|
| 25°C        | 0.0  | 1.0977                                      | 1556.0                 | 3.7627   | 1.7080  | 3.9897                 | 44.94   | 32.09  | ...               | 137.11   |
|             | 0.1  | 1.0979                                      | 1556.5                 | 3.7596   | 1.7088  | 3.9881                 | 44.94   | 32.09  | 7.73              | 136.93   |
|             | 0.2  | 1.0981                                      | 1557.2                 | 3.7555   | 1.7100  | 3.9859                 | 44.94   | 32.09  | 8.97              | 136.76   |
|             | 0.3  | 1.0983                                      | 1558.4                 | 3.7490   | 1.7116  | 3.9825                 | 44.94   | 32.09  | 11.36             | 136.49   |
|             | 0.4  | 1.0985                                      | 1559.2                 | 3.7445   | 1.7128  | 3.9801                 | 44.94   | 32.09  | 11.32             | 136.30   |
|             | 0.5  | 1.0986                                      | 1560.2                 | 3.7394   | 1.7140  | 3.9774                 | 44.95   | 32.10  | 11.57             | 136.10   |
|             | 0.6  | 1.0988                                      | 1561.0                 | 3.7349   | 1.7152  | 3.9750                 | 44.95   | 32.09  | 11.57             | 135.91   |
| 35°C        | 0.0  | 1.0885                                      | 1521.0                 | 3.9711   | 1.6556  | 4.1735                 | 44.98   | 32.12  | ...               | 145.93   |
|             | 0.1  | 1.0886                                      | 1522.2                 | 3.9645   | 1.6571  | 4.1700                 | 44.98   | 32.13  | 15.59             | 145.61   |
|             | 0.2  | 1.0887                                      | 1523.6                 | 3.9569   | 1.6587  | 4.1660                 | 44.99   | 32.13  | 16.76             | 145.31   |
|             | 0.3  | 1.0888                                      | 1525.0                 | 3.9492   | 1.6604  | 4.1620                 | 45.00   | 32.14  | 17.22             | 145.02   |
|             | 0.4  | 1.0889                                      | 1526.4                 | 3.9416   | 1.6621  | 4.1579                 | 45.01   | 32.14  | 17.37             | 144.72   |
|             | 0.5  | 1.0890                                      | 1527.4                 | 3.9361   | 1.6633  | 4.1550                 | 45.02   | 32.15  | 16.47             | 144.51   |
|             | 0.6  | 1.0891                                      | 1528.6                 | 3.9296   | 1.6648  | 4.1516                 | 45.03   | 32.15  | 16.26             | 144.25   |
| 45°C        | 0.0  | 1.0782                                      | 1482.8                 | 4.2182   | 1.5987  | 4.3783                 | 45.03   | 32.15  | ...               | 156.49   |
|             | 0.1  | 1.0783                                      | 1483.4                 | 4.2144   | 1.5995  | 4.3764                 | 45.03   | 32.15  | 13.91             | 156.29   |
|             | 0.2  | 1.0784                                      | 1483.9                 | 4.2112   | 1.6002  | 4.3747                 | 45.03   | 32.15  | 11.62             | 156.17   |
|             | 0.3  | 1.0785                                      | 1484.4                 | 4.2080   | 1.6015  | 4.3730                 | 45.03   | 32.15  | 12.70             | 156.03   |
|             | 0.4  | 1.0786                                      | 1484.9                 | 4.2047   | 1.6016  | 4.3713                 | 45.03   | 32.15  | 12.41             | 155.90   |
|             | 0.5  | 1.0787                                      | 1485.5                 | 4.2010   | 1.6024  | 4.3694                 | 45.03   | 32.15  | 12.84             | 155.74   |
|             | 0.6  | 1.0788                                      | 1486.0                 | 4.1977   | 1.6031  | 4.3677                 | 45.03   | 32.15  | 12.24             | 155.61   |

Wada's constant have been noticed in DMSO+H<sub>2</sub>O system by other workers[8] in case of polymer solution of aqueous and non-aqueous liquids.

It is clear from Tables (1-5) that the  $S_n$  values vary linearly with concentration in H<sub>2</sub>O and pure DMSO. However in mixtures, it varies nonlinearly with concentration in DMSO + H<sub>2</sub>O mixtures. Further, it has been found that the  $S_n$ -values are larger in H<sub>2</sub>O at all concentrations than that in pure DMSO, which is due to the two lone pairs of electrons available for the interaction in case of H<sub>2</sub>O. Thus, the structures of the polymers, polymer – solvent and polymer – polymer interactions are influenced more profoundly in solvents of different polarity as reported by Shah and Parsania [4]. At higher temperatures,  $S_n$ -values vary nonlinearly with concentration for all the mixtures studied. Similar type of behaviour has also been reported by Rakkapan and Punitha[12] in case of ultrasonic studies of ethyl cellulose in alcohols. Ultrasonic velocity study of chloroform and dichloroethane solutions of cardopolysulfone of 1,1'-bis (3-methyl-4-hydroxy-phenyl) cyclohexane and 4,4'-difluorodiphenyl sulfone by Kamani and Parsania [15] reveals

that there occur strong polymer solvent interactions and is supported by positive value of solvation number ( $S_n$ ).  $S_n$ -values show almost negligible variation with concentration.

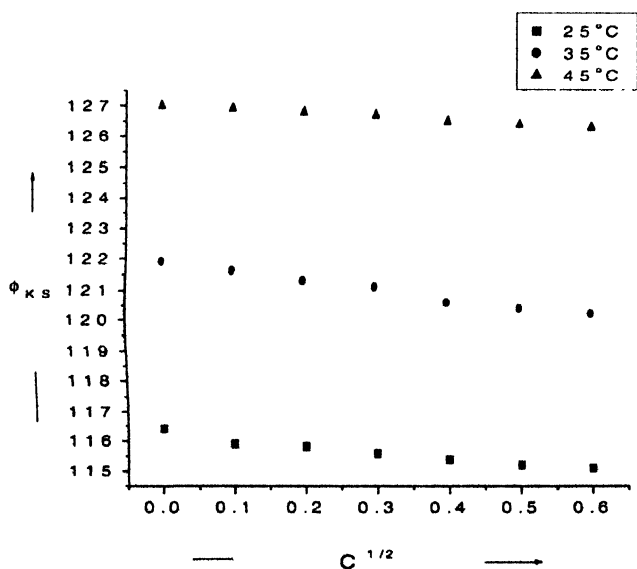
The calculated values of  $\phi_{\lambda}$  of PVP have been presented in Tables (1-5) in DMSO, H<sub>2</sub>O and all the studied mixtures. From the tables, it is clear that  $\phi_{\lambda}$ -values show a gradual decrease with increase in solute concentration in all the studied mixtures (water + DMSO) including pure solvents.

This type of behaviour is similar to that as reported by Syal *et al* [16] for tetra alkylammonium salts in AN+ dioxane systems. The apparent molar adiabatic compressibility ( $\phi_{\lambda}$ ) has been plotted (Figure 2) for PVP in water + DMSO mixtures against square root of concentration *ie*  $\phi_{\lambda}$  vs  $\sqrt{C}$ .  $\phi_{\lambda}$  and  $S_n$  have been evaluated from these plots at different temperatures in accordance with the least square computer program and has been reported in Table 6.

The calculated values of  $\phi_{\lambda}$  presented in Table 6 for PVP in DMSO + H<sub>2</sub>O at different temperatures are all positive indicating the presence of solute-solvent interactions.

**Table 5.** wt% age (w/v), ultrasonic velocity (U), density ( $\rho$ ), adiabatic compressibility ( $\beta$ ), specific acoustic impedance (Z), inter molecular length ( $L_f$ ), relative association ( $R_f$ ), molar sound velocity (R), Wada's constant (W), solvation number ( $S_n$ ) and apparent molar adiabatic compressibility ( $\phi_{\text{AS}}$ ) of PVP in 100 mol % DMSO different temperatures.

| Temperature | w/v% | $\rho \times 10^3$<br>Kg m <sup>-3</sup> | U<br>m s <sup>-1</sup> | $\beta \times 10^{10}$<br>m <sup>2</sup> N <sup>-1</sup> | $Z \times 10^6$<br>Kg m <sup>-2</sup> s <sup>-1</sup> | $L_f \times 10^{11}$ m | $R \times 10^2$<br>m <sup>10/3</sup> s <sup>-1/3</sup> | $W \times 10^{11/7}$<br>m <sup>19/7</sup> N <sup>1/7</sup> | $S_n \times 10^{-2}$ | $\phi_{\text{AS}} \times 10$<br>m <sup>3</sup> s <sup>2</sup> kg |
|-------------|------|--|------------------------|--|---|------------------------|--|--|----------------------|--|
| 25°C        | 0.0  | 1.0954                                   | 1490.9                 | 4.1071   | 1.6331  | 4.1683                 | 81.48  | 58.29  | ---                  | 149.97   |
|             | 0.1  | 1.0955                                   | 1493.8                 | 4.0907   | 1.6364  | 4.1600                 | 81.53  | 58.32  | 20.42                | 149.21   |
|             | 0.2  | 1.0956                                   | 1494.6                 | 4.0860   | 1.6374  | 4.1576                 | 81.53  | 58.33  | 13.12                | 149.07   |
|             | 0.3  | 1.0957                                   | 1495.6                 | 4.0802   | 1.6387  | 4.1546                 | 81.54  | 58.33  | 11.14                | 148.86   |
|             | 0.4  | 1.0959                                   | 1496.8                 | 4.0729   | 1.6403  | 4.1509                 | 81.55  | 58.34  | 10.62                | 148.5  |
|             | 0.5  | 1.0961                                   | 1497.8                 | 4.0667   | 1.6417  | 4.1478                 | 81.55  | 58.34  | 10.02                | 148.37   |
|             | 0.6  | 1.0962                                   | 1498.8                 | 4.0609   | 1.6430  | 4.1448                 | 81.56  | 58.35  | 9.54                 | 148.11   |
| 35 °C       | 0.0  | 1.0854                                   | 1454.1                 | 4.3573   | 1.5783  | 4.3717                 | 81.55  | 58.34  | ---                  | 160.58   |
|             | 0.1  | 1.0856                                   | 1455.4                 | 4.3488   | 1.5800  | 4.3674                 | 81.55  | 58.34  | 9.97                 | 160.15   |
|             | 0.2  | 1.0858                                   | 1456.2                 | 4.3432   | 1.5811  | 4.3646                 | 81.55  | 58.34  | 8.26                 | 159.9  |
|             | 0.3  | 1.0859                                   | 1457.5                 | 4.3350   | 1.5827  | 4.3605                 | 81.57  | 58.35  | 8.71                 | 159.61   |
|             | 0.4  | 1.0860                                   | 1458.8                 | 4.3269   | 1.5843  | 4.3564                 | 81.59  | 58.36  | 8.89                 | 159.26   |
|             | 0.5  | 1.0861                                   | 1459.7                 | 4.3212   | 1.5854  | 4.3535                 | 81.60  | 58.37  | 8.44                 | 159.1  |
|             | 0.6  | 1.0862                                   | 1461.0                 | 4.3131   | 1.5869  | 4.3495                 | 81.62  | 58.37  | 8.60                 | 158.76   |
| 45°C        | 0.0  | 1.0751                                   | 1420.7                 | 4.6084   | 1.5274  | 4.5764                 | 81.69  | 58.43  | ---                  | 171.46   |
|             | 0.1  | 1.0753                                   | 1422.0                 | 4.5991   | 1.5291  | 4.5718                 | 81.71  | 58.43  | 10.32                | 170.92   |
|             | 0.2  | 1.0755                                   | 1422.8                 | 4.5931   | 1.5302  | 4.5688                 | 81.71  | 58.43  | 8.48                 | 170.75   |
|             | 0.3  | 1.0756                                   | 1425.0                 | 4.5785   | 1.5327  | 4.5615                 | 81.74  | 58.45  | 11.04                | 170.16   |
|             | 0.4  | 1.0757                                   | 1426.4                 | 4.5691   | 1.5344  | 4.5568                 | 81.75  | 58.46  | 10.87                | 169.86   |
|             | 0.5  | 1.0759                                   | 1428.0                 | 4.5580   | 1.5364  | 4.5513                 | 81.77  | 58.47  | 11.14                | 169.36   |
|             | 0.6  | 1.0760                                   | 1430.0                 | 4.5448   | 1.5387  | 4.5447                 | 81.81  | 58.49  | 11.71                | 168.85   |



**Figure 2.** Plot of apparent molar adiabatic compressibility ( $\phi_{\text{KS}}$ ) versus  $C^{1/2}$  of PVP in 25 mol% DMSO at different temperatures.

**Table 6.** Limiting apparent molar adiabatic compressibility ( $\phi_{\text{AS}}^0$ ) slope  $S_K$  for PVP in water, DMSO and DMSO + H<sub>2</sub>O mixture different temperatures.

| Mol %<br>DMSO | 25 °C                               |                      | 35 °C                               |                      | 45 °C                               |                      |
|---------------|-------------------------------------|----------------------|-------------------------------------|----------------------|-------------------------------------|----------------------|
|               | $\phi_{\text{AS}}^0 \times 10^{10}$ | $S_K \times 10^{10}$ | $\phi_{\text{AS}}^0 \times 10^{10}$ | $S_K \times 10^{10}$ | $\phi_{\text{AS}}^0 \times 10^{10}$ | $S_K \times 10^{10}$ |
| 0.0           | 179.10                              | -3.05                | 175.29                              | -5.61                | 170.34                              | -4.7                 |
| 25.0          | 116.70                              | -2.07                | 122.62                              | -3.11                | 127.34                              | -1.1                 |
| 50.0          | 125.06                              | -2.42                | 133.46                              | -5.37                | 138.61                              | -1.1                 |
| 75.0          | 137.71                              | -2.27                | 146.61                              | -2.98                | 156.81                              | -1.1                 |
| 100.0         | 150.11                              | -2.47                | 161.19                              | -3.00                | 172.66                              | -4.7                 |

In pure solvent system,  $\phi_{\text{AS}}$  values decrease with increase DMSO content up to 25 mol % DMSO in DMSO + H<sub>2</sub>O mixture and then increase with the further increase of DMSO in DM + H<sub>2</sub>O mixtures. Also, with the increase of temperatures, the values increase slightly in magnitude.

**Conclusions**

From the above observations, it can be concluded that solut

solvent interactions are present in this system, maximized at the same region where solvent-solvent interactions happen to be at their maximum. Furthermore, polymer acts as structure maker in binary mixtures of water and DMSO over the whole solvent composition range.

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