# Densities and viscosities of Binary Mixtures of Polyvinyl Pyrrolidone and Water at Temperatures (288.15 to 313.15) K

## Abstract

Viscosities and densities of polyvinyl pyrrolidone + Water (PVP / $H_2O$) mixtures were measured at several temperatures between (288.15 and 313.15) K under atmospheric pressure. The measured compression factor was satisfactorily correlated by a simple third-order polynomial with respect to temperature. The adjustment parameters are determined and presented. The comparison of correlated and experimental results indicated the applicability of the proposed model for compressibility factor predication of (PVP / $H_2O$) mixtures.

**Keywords:** Viscosity**;** density**;** polyvinyl pyrrolidone; compression factor

## 1. Introduction

Polyvinyl Pyrrolidone (PVP) is an important member of the polymers family with excellent physical properties. It was one of the first polymers to be developed, and the products it provides are essential components of a sustainable society. PVP is soluble in water and other polar solvents. When dry it is a light flaky hygroscopic powder, readily absorbing up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings.[1-3] PVP is also used in many technical applications as an adhesive in glue stick and hot-melt adhesives as a special additive for batteries, ceramics, fiberglass, inks, and inkjet paper, and in the chemical-mechanical planarization process as an emulsifier and disintegrant for solution polymerization to increase resolution in photoresists for cathode ray tubes (CRT) in aqueous metal quenching for production of membranes, such as dialysis and water purification filters as a binder and complxation agent in agro applications such as crop.[4-7]

One of the most important properties of polyvinyl pyrrolidone and polyvinyl pyrrolidone solvent mixtures are their ability to flow under the action of applied conditions at different temperatures. The quantitative evaluation of flow behavior in terms of applied density and temperatures is a great practical importance and theoretical interest.[8-11]

Properties of PVP have been examined in various solvents. Water is utilized as a solvent in numerous PVP adhesives. Water is also used in recovery and recycling of PVP or extraction of polymers. Therefore, solubility and flow behavior of PVP solvent mixtures are important in application of PVP. The interaction between PVP and Water molecules causes a linear increase of density and viscosity of PVP / Water mixtures with an increase of PVP concentration in the Water.[9,10] The flow behavior of PVP / Water mixtures can be studied by viscometric measurements. The viscosity of these mixtures and in general the viscosity of polymer solvent mixtures are highly dependent on the density and temperature of the polymer. Fortunately, viscosity measurements of polymer solvent mixtures provide an efficient method for determination of the compression factor $z$ of the polymer. [8,12]

Hence, we report in this paper the experimental values of densities and viscosities for the binary mixtures of PVP/$H_2O$ over the entire range of compositions at $T$ (288.15, 293.15, 298.15, 303.15, and 313.15) K and $p = 0.1$ MPa. From the measured densities data, the compression factor, have been calculated at each temperature. Temperature dependency of compression factor of PVP in $H_2O$ has also been calculated. The derived functions, $z$ , $(\partial z/\partial T)_\rho$ and $(\partial^2 z/\partial T^2)_\rho$, have been used to gain a better understanding of the intermolecular interactions between the component molecules of the liquid mixtures.[8] We have chosen thermodynamic methods for this study, as these methods are important because changes in properties of the system caused by variations of temperature and composition can be studied without any reference to assumptions, models, or hypotheses.[13]

## 2. Experimental Section

Commercial grade PVP was provided by Merck Company. The PVP/$H_2O$ mixtures were prepared by mass, using a digital balance (A&D Company, model GF-300) with an uncertainty of $\pm 0.0006$ g.[14-17] Caution was taken to prevent the evaporation of the solutions after preparation. The calibration was performed in comparison with standard reference IDS 311. This calibration is traceable able to BNW. Density measurements of binary mixtures were performed at atmospheric pressure at at $T$ (288.15, 293.15, 298.15, 303.15, and 313.15) K by means of a vibrating-tube density meter firmware version V1.003 (model: DMA 500, Anton Paar) which was calibrated with distilled water and air. The apparatus was calibrated once a day with dry air and double-distilled freshly degassed water. Kinematic viscosities, $v(=\eta/\rho)$ of the PVP/$H_2O$ mixtures were measured using a calibrated modified Ostwald viscometer (Cannon-fenske glass capillary viscometers, CFRU, CFRC Series, 50CC) with inner diameters of (0.40±2) % mm. The flow time was measured with a stop watch capable of recording to 0.01 s. For each solution, the experimental viscosity was obtained by averaging two to three flow time measurements.[17-21]

The measurements of solution viscosity in terms of flow time would account for the kinetic energy of the moving liquid. Considering the kinetic energy, the viscometer was calibrated by the following equation

$$\frac{\eta}{\rho} = kt - \frac{L}{t} \tag{1}$$

Where $\eta$ is the absolute viscosity; $\rho$ is the density; and $t$ is the flow time of the pure calibration liquid. $k$ and $L$ were the characteristic viscometer constants. The kinetic energy term in eq1, $(L/t)$, is an important term in viscosity calculations if the liquid is moving fast ($t$ is small), but if the flow is slow ($t$ is large), the kinetic energy term, which is proportional to $(1/t)$, can be ignored.[21] In this work by using the absolute viscosity and density $\rho$ of pure water, the characteristic viscometer constants $k$ and $L$ were obtained. The accuracy of the used densitometer and viscometer was tested with the density and viscosity measurements of pure water at 303 K and 313K. Table1 shows the obtained experimental results for the density and flow time measurements. In this table, the obtained data were compared with the available data in the literature. These comparisons indicated good consistency between these results and those presented in the literature. The flow time, viscosities and Kinematic viscosities for the binary mixtures studied at (303.15, and 313.15) K are reported in Tables 2 &3.

## 3. Effect of Temperature on Density.

The experimental density, $\rho$, versus composition data of (PVP+$H_2O$) mixtures at different temperatures are listed in Table 4. The densities for the system (PVP+$H_2O$) supposed to be measured in temperatures higher than 288.15 K, which can provide experimental error, problem with two phases in the syringe at room temperature and with injection to the apparatus. This was the reason that the experimental densities and excess molar volumes for the mixture of

(PVP+$H_2O$) were not determined. As usual, density decreases with increasing temperature for pure substances and for the mixtures. We find new data in binary systems as a function of temperature for comparison. A second-order polynomial was found to satisfactorily correlate the change of density with temperature for (PVP+$H_2O$) mixtures.[22] The graphical variation of density as a function of temperature, for the binary mixtures of PVP+$H_2O$ at $C$=5g.L$^{-1}$ is presented in Figure1.

## 4. Effect of Temperature on Compressibility factor

Liquids and dense fluids are usually considered to be complicated on a molecular scale, and a satisfactory theory of liquids only began to emerge in the 1960s.' However, they show a number of simple regularities, some of which have been known for years without any theoretical basis.[13,23,24] We mention just three examples. The first is the Tait-Murnaghan relation, known for over 100 years, in which the bulk modulus (reciprocal compressibility) of a liquid (or solid) is linear in the pressure. The second is the linear relation between temperature and density at unit compression factor ($Z=pv/RT$ = l), discovered empirically in 1906, then forgotten and rediscovered several times, and recently christened the 'Zeno line. The compression factor is one of the most important fundamental properties; it is closely related to various properties, such as thermal pressure coefficient, isothermal compressibility, and isobaric expansibility. Thus, the study of compression factor could provide a useful basis for understanding the nature of liquid. Since it is normally difficult to obtain the properties by thermodynamic and statistical mechanics methods due to complex interactions among molecules, experimental methods have attracted much attention.[12]

We have chosen experimental method for this study, as these methods are important because changes in compression factor of the system caused by variations of temperature and composition can be studied without any reference to assumptions, models, or hypotheses. The compression factor versus composition data of (PVP+$H_2O$) mixtures at different temperatures are listed in Table 4. The compression factor for the system (PVP+$H_2O$) supposed to be measured in temperatures. As usual, compression factor decreases with increasing temperature for (PVP+$H_2O$) mixtures. The graphical variation of compression factor as a function of temperature, for the binary mixtures of PVP+$H_2O$ at $C$=1g.L$^{-1}$ is presented in Figure2. We find new data in (PVP+$H_2O$) binary systems as a function of temperature for comparison. A third-order polynomial was found to satisfactorily correlate the change of density with temperature for (PVP+$H_2O$) mixtures, where $T$ is for the absolute temperature and $A_{ij}$, $B_{ij}$, $C_{ij}$ and $D_{ij}$ refer to the fit coefficients.[9]

$$z_{ij} = A_{ij} + B_{ij}T + C_{ij}T^2 + D_{ij}T^3 \tag{2}$$

$$\left(\frac{\partial z_{ij}}{\partial T}\right)_{\rho_{ij}} = T + 2C_{ij}T + 3D_{ij}T^2 \tag{3}$$

$$\left(\frac{\partial^2 z_{ij}}{\partial T^2}\right)_{\rho_{ij}} = 2C_{ij} + 6D_{ij}T \tag{4}$$

Fit parameters are listed in Table 5. Because compression factor is subject to experimental error, we measure the goodness of fit by the coefficient of determination $\boldsymbol{R^2}$, which is the square of the correlation coefficient. In the present cases, $\boldsymbol{R^2}$ should be within 0.005 of unity for the fit to be considered good.[23,24]

## 5. Results and Discussion

Thermodynamic and transport properties, such as density and viscosity, of dense fluids are important design and process information to the petroleum industry. Density and viscosity are also key properties characterizing oil reservoirs, thus their knowledge will contribute to a more effective exploitation of the reserves of fossil energy.[8-11] More broadly, these two properties are central in the study of any process bringing into play fluid mechanics and transport phenomena.[19] Asymmetric mixtures contain either specific interactions or large differences in molecular shape, size or flexibility, that cause marked behaviors of their properties. The study of transport properties of such mixtures is also motivated by deficiencies in their present theoretical representation.[8] The actual state of the art in transport property theory and modeling is such that the prediction of the viscosity of a mixture from that of the pure components is still not possible with confidence in the general case. The situation in this field is less advanced than that for most equilibrium thermodynamic properties. The present work aims at producing new results of viscosity and density of a liquid mixture: the binary system (PVP+$H_2O$). This liquid mixture presents a one-phase envelope spanning a wide composition range at room temperature and atmospheric pressure, and may require a temperature of as much as 313K to exist as a single fluid phase at atmospheric pressure.[22] Its handling is therefore significantly more complicated than that of simply liquids. The experimental setup used in the present work has been specially adapted to liquid mixtures. The sample is introduced into a u-shaped borosilicate glass tube that is being excited to vibrate at its characteristics frequency. The characteristics frequency changes depending on the density of the sample. Through a precise determination of the characteristic frequency the density of the sample can be calculated. Due to the temperature dependency of the density value, a precise temperature control of the sample is required. In binary mixtures, the density of the mixture is a function of its composition. Thus, by using density/concentration tables, the density value of a binary mixture can be used to calculate its composition. The adjustment media are dry air and freshly degassed ultra pure (bi-distilled or deionized) water.

## 6. Conclusion

The present work presents an application of the technique of simultaneous viscometry and densimetry, using a vibrating-wire sensor, to the study of a model liquid fluid. The model system in question is a binary mixture of PVP and $H_2O$, two molecules of the different family having marked size and flexibility differences. From a methodological point of view, the main conclusion regards the suitability of the technique to this kind of high-temperature work requiring an accurate method, based on well described physical principles. The absence of extensive calibration procedures and the simultaneous nature of the measurements are advantages in terms of productivity. Handling the model liquid mixtures was no more complex than with any other viscometry technique. Concerning the results, they agree well with measurements of several other authors, obtained using different kinds of experimental method.

In this work, the viscosity of polyvinyl pyrrolidone + Water mixtures was measured by a model proposed by the authors. According to the kinematic viscosity model the density and PVP concentration, $C$ of polyvinyl pyrrolidone + Water mixtures were measured and evaluated with respect to temperature. The compressibility factor of the PVP sample was also determined by measurements of the accurate density of polyvinyl pyrrolidone + Water mixtures and correlated by a third-order polynomial with respect to polyvinyl pyrrolidone + Water mixtures temperature, $T$, and the evaluated parameters were reported. The parameters of the compressibility factor were calculated and reported. The values $R^2$ reported in Table5 indicate the high quality of fitting according to eq2.

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**Table1. Comparison of Densities ( $\rho$ ) of Pure Components with Literature Values of $H_2O$**

| **$T$ / K** | $\rho_{\mathrm{Exp}}$ / g.cm$^{-3}$ | **Flow Time / Sec** | $\rho_{\mathrm{Cal}}$ / g.cm$^{-3}$ |
|---|---|---|---|
| 303.15 | 0.9950 | 247.20 | 0.9957 |
| 313.15 | 0.9910 | 249.60 | 0.9923 |

**Table2. Measured absolute viscosity and kinematic viscosity of the PVP/H2O Mixtures at 303.15 K for five different Polymer Concentrations**

| $T$ / K | $C$ / g.L$^{-1}$ | Flow Time / Sec | $\eta$ / cP | $v$ |
|---|---|---|---|---|

| | | | | |
|---|---|---|---|---|
| 303.15 | 1.0000 | 253.0100 | 0.8195 | 0.8228 |
| 303.15 | 1.4000 | 253.3000 | 0.8196 | 0.8238 |
| 303.15 | 2.0000 | 254.5000 | 0.8210 | 0.8277 |
| 303.15 | 4.0000 | 256.1200 | 0.8288 | 0.8329 |
| 303.15 | 5.0000 | 257.1300 | 0.8329 | 0.8362 |

**Table3. Measured absolute viscosity and kinematic viscosity of the PVP/H2O Mixtures at 313.15 K for five different Polymer Concentrations**

| $T$ / K | $C$ / g.L$^{-1}$ | Flow Time/Sec | $\eta$ / cP | $v$ |
|---|---|---|---|---|
| 313.15 | 1.0000 | 257.0000 | 0.6749 | 0.6804 |
| 313.15 | 1.4000 | 257.5000 | 0.6769 | 0.6817 |
| 313.15 | 2.0000 | 260.0100 | 0.6828 | 0.6883 |
| 313.15 | 4.0000 | 263.5500 | 0.6921 | 0.6977 |
| 313.15 | 5.0000 | 266.1200 | 0.6989 | 0.7045 |

**Table4. Measured Density, compression factor and temperature derivatives of compression factor for PVP/H2O Mixtures at Different Temperatures and Concentrations**

| **T / K** | **$C$ / g.L$^{-1}$** | **$\rho$ / kg.L$^{-1}$** | **$z$ / mol.kg$^{-1}$** | **$\partial z / \partial T$** | **$\partial^2 z / \partial T^2$** |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| 288 | 1.0000 | 0.9980 | 0.0424 | -1.3122e-4 | -1.5708e-6 |
| 293 | 1.0000 | 0.9970 | 0.0417 | -1.3610e-4 | -3.7943e-7 |
| 298 | 1.0000 | 0.9960 | 0.0411 | -1.3502e-4 | 8.1199e-7 |
| 303 | 1.0000 | 0.9960 | 0.0404 | -1.2798e-4 | 2.0034e-6 |
| 313 | 1.0000 | 0.9920 | 0.0393 | -9.6032e-5 | 4.3862e-6 |
| 288 | 2.0000 | 0.9990 | 0.0424 | -1.6361e-4 | 8.9017e-6 |
| 293 | 2.0000 | 0.9980 | 0.0417 | -1.2778e-4 | 5.4304e-6 |
| 298 | 2.0000 | 0.9970 | 0.0410 | -1.0931e-4 | 1.9590e-6 |
| 303 | 2.0000 | 0.9920 | 0.0406 | -1.0819e-4 | -1.5123e-6 |
| 313 | 2.0000 | 0.9920 | 0.0393 | -1.5803e-4 | -8.4550e-6 |
| 288 | 4.0000 | 0.9990 | 0.0424 | -1.3017e-4 | 1.9801e-7 |
| 293 | 4.0000 | 0.9980 | 0.0417 | -1.2876e-4 | 3.6597e-7 |
| 298 | 4.0000 | 0.9950 | 0.0411 | -1.2651e-4 | 5.3394e-7 |
| 303 | 4.0000 | 0.9950 | 0.0405 | -1.2342e-4 | 7.0190e-7 |
| 313 | 4.0000 | 0.9920 | 0.0393 | -1.1472e-4 | 1.0378e-6 |
| 288 | 5.0000 | 0.9990 | 0.0424 | -1.3685e-4 | 2.2320e-7 |
| 293 | 5.0000 | 0.9980 | 0.0417 | -1.3458e-4 | 6.8705e-7 |
| 298 | 5.0000 | 0.9970 | 0.0410 | -1.2998e-4 | 1.1509e-6 |
| 303 | 5.0000 | 0.9960 | 0.0404 | -1.2307e-4 | 1.6147e-6 |
| 313 | 5.0000 | 0.9920 | 0.0393 | -1.0228e-4 | 2.5424e-6 |

**Table5. Parameters of the Compressibility factor, Equation 3, for the PVP/$H_2O$ Mixtures**

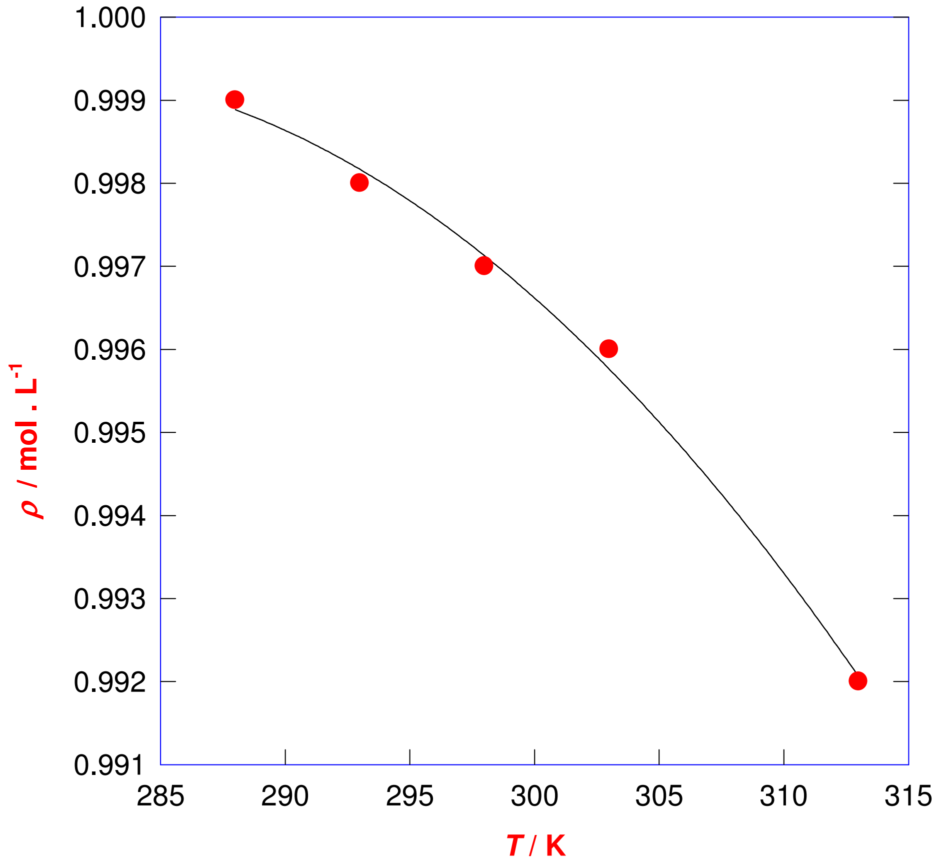
| $C$ / g.L$^{-1}$ | $A$ | $B$ | $C$ | $D$ | $R^2$ |
|---|---|---|---|---|---|
| 1.0000 | -0.9336 | 0.0102 | -3.5098e-5 | 3.9714e-8 | 1.0000 |
| 1.4000 | 0.4923 | -4.1714e-3 | 1.3174e-5 | -1.4286e-8 | 1.0000 |
| 2.0000 | 3.2228 | -0.0315 | 1.0443e-4 | -1.1571e-7 | 0.9994 |
| 4.0000 | -0.0457 | 1.2060e-3 | -4.7384e-6 | 5.5988e-9 | 0.9996 |
| 5.0000 | -0.2783 | 3.6462e-3 | -1.3247e-5 | 1.5462e-8 | 1.0000 |
| 6.0000 | -0.3804 | 4.5937e-3 | -1.6155e-5 | 1.8408e-8 | 0.9998 |

## Figure Capture

**Figure 1.** The density versus temperature for the PVP+$H_2O$ binary system at $C$ = 5g.L$^{-1}$.

**Figure 2.** The compression factor versus temperature for the PVP+$H_2O$ binary system at different densities.

**Fig.1**



1.000
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0.998
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285
290
295
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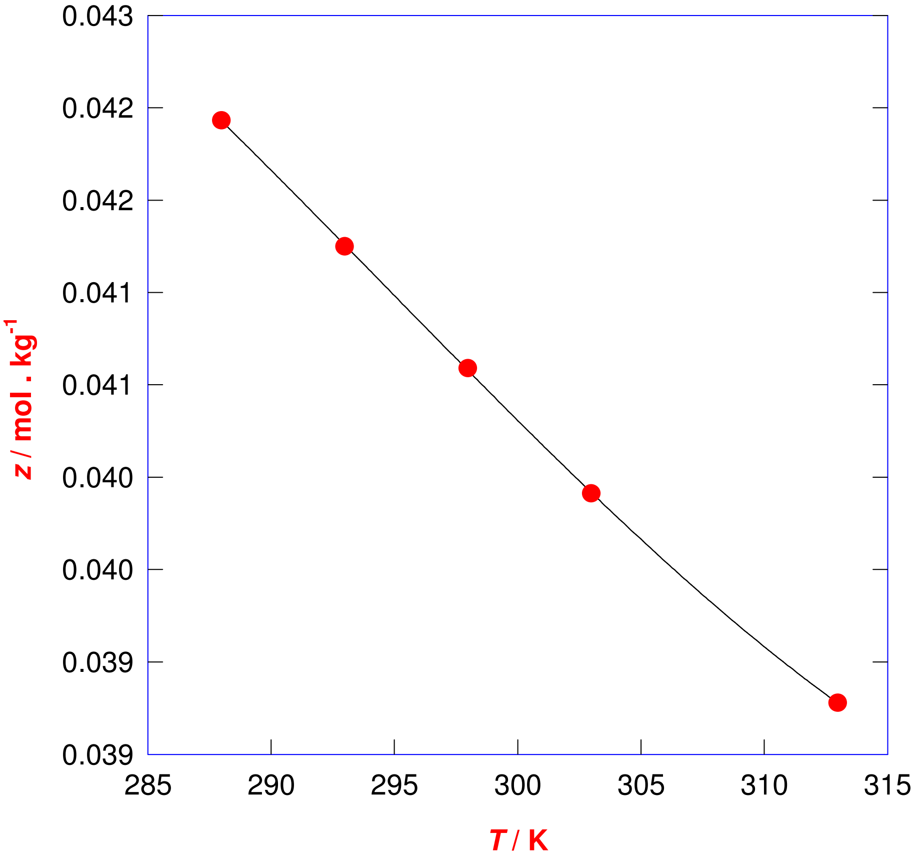
310
315
$\rho$ / mol . L$^{-1}$
$T$ / K

**Fig.2**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