# Experimental measurements and modelling of the solvent activity and surface tension of binary mixtures of poly(vinyl pyrrolidone) in water and ethanol

MAJID TAGHIZADEH* and SABER SHEIKHVAND AMIRI

*Chemical Engineering Department, Babol Noshirvani University of Technology, P. O. Box 484, Babol 4714871167, Iran*

*Abstract*: In this paper, the density ($\rho$), viscosity ($\eta$) and surface tension ($\sigma$) of solutions of poly(vinyl pyrrolidone) (PVP) with molecular weights of 25000 (K25) and 40000 g mol$^{-1}$ (K40) in water and ethanol were measured in the temperature range 20–65 °C and at various mass fractions of polymer (0.1, 0.2, 0.3 and 0.45). The solvent activity measurements were performed at 45 and 55 °C. Thereafter, two thermodynamic models for predicting the solvent activity and surface tension of binary polymer mixtures (PVP in water and ethanol) were proposed. The Flory–Huggins theory and Eyring model were employed to calculate the surface tension of the solution and the solvent activity, respectively. Additionally, the proposed activity model was dependent on the density and viscosity of the solution. Afterwards, the ability of these models at various temperatures and mass fractions were investigated by comparing the results with the experimental data. The results confirmed that, in the investigated temperature range, these models have good accuracy.

*Keywords*: poly(vinyl pyrrolidone); solvent activity; surface tension; thermosdynamic model.

## INTRODUCTION

Considering the importance of density, viscosity and the activity of pure liquids and mixtures in various fields of chemical engineering, such as, environmental engineering, pharmaceuticals, paint and detergents, lubricants, catalytic reactions, liquid extraction, petroleum refining and other processes involving heat and mass transfer, measuring these parameters and providing a model in a temperature range with an acceptable response have been discussed in the literature.[1–9] In recent years, aqueous polymer solutions have exhibited a wide range of applications in different industries. Poly(vinyl pyrrolidone) (PVP) is one of the

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most important polymers, which is used as a blood plasma expander due to its low toxicity.[2,3]

Surface tension is one of the important properties of binary polymeric mixtures in various fields of applied science. Surface tension is a physical property that is closely related to the molecular composition and structure.[10–12] Surface tension of pure fluids and mixtures can usually be measured directly, but the lack of resources and facilities makes the experimental measurements of the surface tension of a liquid difficult and impractical. Therefore, an estimation method for the surface tension of polymeric mixtures is required if it is not possible to determine reliable experimental values.[13,14] The surface tension of liquids can be measured by the drop-weight method,[15] the Wilhelmy plate or ring method,[16,17] and the maximum bubble pressure method.[18] The ring method is one of the most common methods used for the measurement of surface tension. The advantages of the ring method are that it is fast and simple and does not require calibration using solutions with known surface tension.

Many models have been developed to predict the thermodynamic properties of binary mixtures. Some researchers proposed theoretical methods to calculate the surface tension based on thermodynamics.[19] Egemen *et al.*[20] proposed a group contribution method to predict the surface tension of liquid organic solvents. Polymer solution thermodynamics usually has its origin in the thermodynamics of mixtures of quasi-spherical molecules. This field has been proliferating along with polymer activity models.[21–24]

The activity of a pure substance, or of a specified component in a solution, is commonly defined in terms of fugacity, the activity of the material or component being the ratio of its fugacity in the given state to that in some "standard state" at the same temperature.[25] Solvent activity is an effective parameter in various fields and processes, such as the prediction of the crystallization of solids that have water of hydration. There are several methods to measure the solvent activity of mixtures, such as freezing point depression, boiling point elevation, dynamic and static vapour pressure measurements, osmotic pressure measurements, hygrometric, vapour sorption, isopiestic method and vapour pressure osmometry (VPO). Among the methods mentioned, vapour pressure osmometry is a precise technique to determine the solvent activity of solutions.[26]

In this study, the density, viscosity and surface tension of solutions of poly-(vinyl pyrrolidone) (PVP) with molecular weights of 25,000 (K25) and 40,000 g mol$^{-1}$ (K40) in water and ethanol were measured in the temperature range 20–65 °C. Solvent activity measurements were performed at 45 and 55 °C using the vapour pressure osmometry (VPO) technique. All measurements were performed in binary systems containing of 0.1, 0.2, 0.3 and 0.45 mass fractions of polymer. For the systems studied, two thermodynamic models were also developed for calculating the solvent activity, and the surface tension of PVP solutions based on

Eyring model[27] and Flory–Huggins[28] theory, respectively. The activity model was dependent on the density and viscosity of solution. Next, the surface tensions of solutions and solvent activities for polymer/solvent mixtures were calculated and compared with the experimental values.

## EXPERIMENTAL

*Materials*

Poly(vinyl pyrrolidone) (PVP) with molecular weights of 25000 and 40000 g mol$^{-1}$ and absolute ethanol GR (>99 %), manufactured by Merck, were used in this study. Double-distilled water was used to produce the solutions.

*Apparatus and procedures*

The solutions were prepared by mass, using Sartorius balance with an accuracy of ±0.1 mg. The density, viscosity, surface tension and activity measurements were realised using a pycnometer, a DV-II + Pro digital viscometer manufactured by Brookfield (USA), a digital tensiometer Kruss k9 (Hamburg, Germany), and a vapour pressure osmometer (VOP) (Knauer, Germany), respectively. The tensiometer, which was equipped with a Du Noüy platinum–iridium ring (6 mm circumference), was calibrated with distilled water ($\sigma$ = 72.8 mN m$^{-1}$). A constant temperature water bath was used to control the temperature of the solutions with an accuracy of ±0.1 °C. Measurements for each solution were repeated five times.

The density, viscosity, activity and surface tension of the PVP solutions in water and ethanol were measured at different temperatures and concentrations, and the obtained results were correlated with quadratic equations relating the density and viscosity of the solutions to the mass fraction of the polymer.

Several types of errors, *i.e.*, the relative error (*RE*), average relative error (*ARE*), the average absolute relative error (*AARE*) and root mean squared error (*RMSE*), were calculated for evaluating the performance of the proposed model (Supplementary material to this paper).

*Density*

Density measurements were performed using a pycnometer, the bubble volume of which was 25 cm$^3$, at temperatures of 20, 25, 30, 35, 40, 45, 50 and 55 °C. Each measurement was repeated three times and the average results of the density and their corresponding standard deviation values are reported. The following equation was used to determine the density of solution using the experimental data:

$$\rho = a + bw + cw^2 \tag{1}$$

where *w* is the mass fraction of polymer, $\rho$ is density (g cm$^{-3}$), and *a*, *b* and *c* are adjustable parameters that were obtained by linear multiple regression using Statica 7 software. The measured densities of the solutions, the coefficients of Eq. (1) along with its average relative error (*ARE*), coefficient of determination ($R^2$), and root mean squared error (*RMSE*) are reported in Table S-I of the Supplementary material. As can be seen in this Table, the standard deviation values of the results were relatively low and in the range of 0.001–0.003 (g cm$^{-3}$), which show the good reproducibility and accuracy of the experiments.

*Viscosity*

The viscosity measurements were performed three times using the DV-II + Pro digital viscometer manufactured by Brookfield (USA) and the average results and their corresponding standard deviation values are reported. The following equation was used to determine the viscosity of the solutions using the experimental data:

$$\eta = a' + b'w + c'w^2 + d'w^3 \tag{2}$$

where $w$ is the mass fraction of polymer, $\eta$ is viscosity (mPa s), and $a'$, $b'$, $c'$ and $d'$ are adjustable parameters that were obtained by linear multiple regression using STATICA7 software. The measured viscosities of the solutions, the coefficients of Eq. (2) along with its average relative error, coefficient of determination, and root mean squared error are reported in Table S-II of the Supplementary material. As can be seen in this Table, the standard deviation values of the results were relatively low and in the range of 0.1–37 (mPa s), which show the good reproducibility and accuracy of the experiments.

*Solvent activity*

The activity of the solvent in the polymer solution was measured using the vapour pressure osmometry (VOP, Knauer, Germany) method at 45 and 55 °C and at different mass fractions of polymer (0.1, 0.2, 0.3 and 0.45). Before beginning each experiment, the calibration constant of the instrument was determined using a urea–water solution and a phenyl-methanol–ethanol solution. The calibration constants had different values at different temperatures and had to be determined for each temperature. Two thermistors covered with platinum screens pieces were placed in the measuring chamber. In the chamber, a container of solvent provided a saturated solvent atmosphere around thermistors by using two wicks. Usually, if a droplet of solvent is dripped on one of the thermistors and a droplet of solution I dripped on the other thermistor, $\Delta V$ begins to rise. After reaching a state of quasi-equilibrium, it remains almost unchanged. Temperature differences between the two thermistors were reported as voltage differences. The activity was calculated using the following equation:[29]

$$\frac{\Delta V M_1}{1000K} = -\ln a_1 \tag{3}$$

where $a_1$ is the activity of the solvent, $\Delta V$ is the voltage difference, $M_1$ is the molecular weight of the solvent and $K$ is the calibration constant. Each measurement was repeated 3 to 5 times, and the mean of the voltage difference is reported. The accuracy of the measured voltage difference was 0.1 mV.

*Surface tension*

The surface tension measurements were conducted using a Kruss k9 digital tensiometer (Hamburg, Germany). This instrument comprises a precise microbalance and an accurate mechanism to move vertically the liquid sample in a glass beaker. Here, the surface tension of the polymer solutions was measured by the ring method (Du Nouy Method). In the ring method, a mechanical force is required to lift a ring from the liquid surface. The ring is usually made of an alloy of platinum and iridium. Measurements were performed at different temperatures using a warm-water bath; the temperature of the sample was kept at equilibrium. Each measurement was performed three times and the average results of the surface tension and their corresponding standard deviation values are reported.

Thermodynamic models for solvent activity and surface tension are presented in the Supplementary material to this paper.

RESULTS AND DISCUSSION

*Solvent activity*

The proposed thermodynamic model for calculating the solvent activity is a function of mole fraction, mass fraction, density (or specific volume) and visco-

sity of the solution. The density and viscosity of the solutions are expressed as a function of mass fraction of polymer (in the form of a mathematical model). To calculate the solvent activity of the polymer mixtures at the mentioned temperatures and mass fractions, the density and viscosity of the solutions have to be accurately determined because they are crucial for obtaining good results with the proposed model.

The experimental values have been used to validate the model. First, the solvent activities in the polymer–solvent systems were measured by the osmometry method. Then the solvent activities were calculated by the model and the results were compared with the experimental data.

Comparisons between the experimental and calculated solvent activities for various mass fractions at temperatures of 45 and 55 °C are presented in Figs. 1 and 2. Solvent activity values measured for PVP solutions at different tempera-
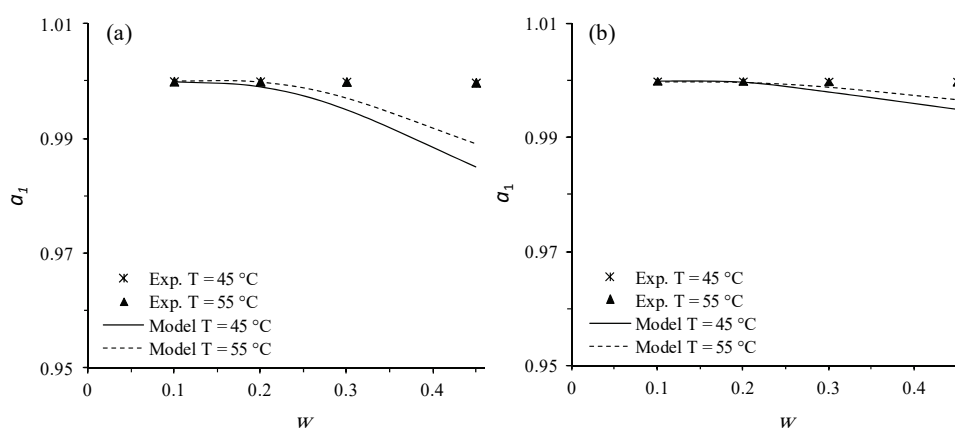


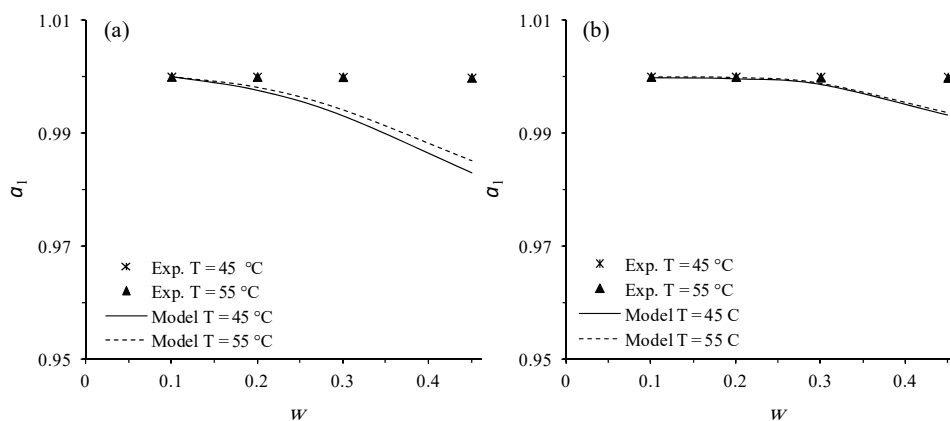Fig. 1. Solvent activity in (a) K25–water; and (b) K25–ethanol solutions at 45 and 55 °C.



Fig. 2. Solvent activity in (a) K40–water, (b) K40–ethanol solutions at 45 and 55 °C.

tures and along with their relative errors and average absolute relative errors are reported in Table S-III of the Supplementary material. As seen in Figs. 1 and 2, the solvent activities decreased significantly with increasing weight percentage of the polymer in the range 0.3–0.45. These results showed that the proposed model could predict with good accuracy the solvent activity in the mass fraction range of 0.1 to 0.3.

*Surface tension*

The surface tensions of polymer solutions were measured using a digital tensiometer at different temperatures and mass fractions of polymer. The surface tension values and relative error percentages along with their average absolute relative errors at various temperatures are given in Table S-IV of the Supplementary material.

A UNIFAC model and the Flory–Huggins solution theory were applied to develop a thermodynamic model to predict the surface tensions of the PVP solutions. Comparisons of the experimental and theoretical results for the PVP–solvent systems are shown in Figs. 3 and 4. In addition, the trends in the evolution of the surface tension with temperature at various mass fractions are illustrated.
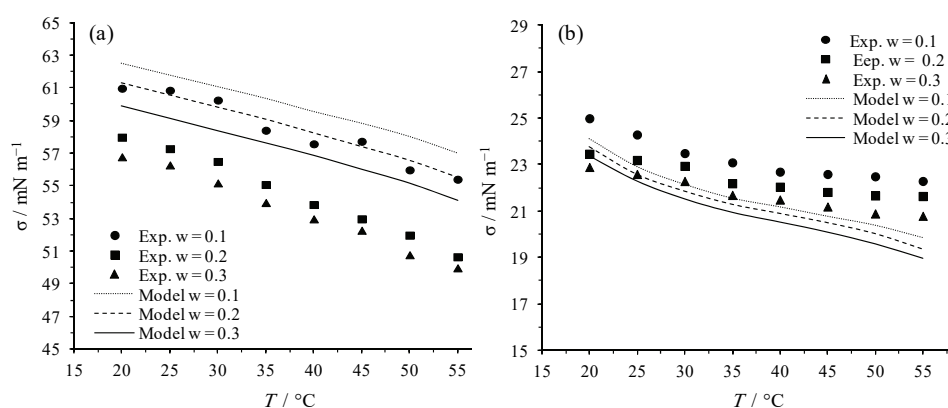


Fig. 3. Surface tension of (a) K25–water; and (b) K25–ethanol solutions at various temperatures.

On increasing the temperature, the force between the molecules is reduced and less force is required to pull the molecules into the liquid. Thus, the surface tension of the liquid is reduced. Moreover, the surface tension can vary due to chemical substances in contact. As could be seen in Figs. 3 and 4, the surface tension decreased with increasing the mass fraction of polymer. The experimental results and the results obtained from the proposed model confirmed the inverse relationship between temperature and mass fraction with the surface tension of the solution.
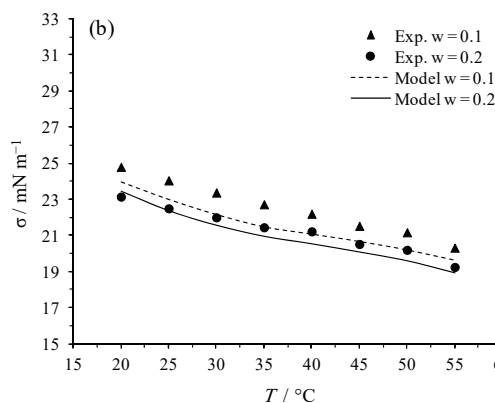
Fig. 4. Surface tension of (a) K40–water; and (b) K40–ethanol solutions at various temperatures.

## CONCLUSIONS

In this study, thermodynamic modelling and experimental procedures were used to study the activity and surface tension of binary polymer mixtures. First, the density, viscosity and surface tension of solutions, and solvent activities of poly(vinyl pyrrolidone) with molecular weights of 25000 and 40000 g mol$^{-1}$ in water and ethanol were measured at different temperatures and mass fractions. Then, two quadratic equations were presented to determine the density and viscosity of solutions as a function of mass fraction. These equations were used to present a thermodynamic model for the prediction of solvent activities. This model was developed based on the Eyring viscosity model. Next, a thermodynamic model based on the Flory–Huggins theory was presented for the prediction of the surface tension of the solutions. The results obtained from the surface tension and activity models for polymer/solvent mixtures were compared with the experimental results. The overall average absolute relative errors of the models for solvent activities and surface tensions of the solutions were estimated to be 0.35 and 5.69 %, respectively. These results show that the proposed thermodynamic models were able to predict the surface tension and activity of the solvent with good accuracy.

## NOMENCLATURE

| | |
|---|---|
| $A$ | Molar surface area (cm$^2$ mol$^{-1}$) |
| $a$ | Activity of solvent |
| $g^{*E}$ | Excess Gibbs free energy (J mol$^{-1}$) |
| $M_1$ | Molecular weight of solvent (g mol$^{-1}$) |
| $Q$ | UNIFAC parameter |
| $R$ | Gas constant (J mol$^{-1}$ K$^{-1}$) |
| $T$ | Absolute temperature (K) |
| $w$ | Mass fraction of polymer |
| $x$ | Mole fraction of component |
| $\gamma$ | Activity coefficient of solvent |

| $\Delta V$ | Voltage difference (mV) |
|---|---|
| $\delta$ | Solubility parameter ($J^{1/2}$ $cm^{-3/2}$) |
| $\eta$ | Viscosity of solution (mPa s) |
| $\mu^{\upsilon}$ | Standard chemical potential ($J$ $mol^{-1}$) |
| $\upsilon$ | Molar volume of solution ($cm^3$ $mol^{-1}$) |
| $\upsilon_k$ | Number of group $k$ |
| $\rho$ | Density of solution (g $cm^{-3}$) |
| $\sigma$ | Surface tension of solution (mN $m^{-1}$) |
| $\phi$ | Volume fraction |
| $\chi$ | Interaction parameter between polymer and solvent |

## SUPPLEMENTARY MATERIAL

Experimental data and theoretical models are available electronically at the pages of the journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

ЕКСПЕРИМЕНТАЛНО ОДРЕЂИВАЊЕ И МОДЕЛОВАЊЕ АКТИВНОСТИ РАСТВАРАЧА И ПОВРШИНСКИХ НАПОНА БИНАРНИХ СМЕША ПОЛИ(ВИНИЛПИРОЛИДОНА) У ВОДИ И ЕТАНОЛУ

MAJID TAGHIZADEH и SABER SHEIKHVAND AMIRI

*Chemical Engineering Department, Babol Noshirvani University of Technology, P. O. Box 484, Babol 4714871167, Iran*

У овом раду су приказани резултати експерименталног мерења густина ($\rho$), вискозности ($\eta$) и површинских напона ($\sigma$) смеша поли(винилпиролидона) (PVP), моларних маса 25000 (K25) и 40000 g $mol^{-1}$ (K40), у води и етанолу у температурном опсегу 20–65 °C и при различитим масеним уделима полимера (0,1, 0,2, 0,3 и 0,45). Мерења површинског напона вршена су на 45 и 55 °C. Такође, предложена су два термодинамичка модела за предвиђање активности растварача и површинског напона бинарних смеша полимера (PVP у води и етанолу). Flory–Huggins и Eyring модели коришћени су за израчунавање површинског напона раствора и активности растварача. Предложени модели зависе од вредности густине и вискозности раствора. Поређењем са експерименталним подацима испитивана је применљивост ових модела на већем броју температура и више масених удела. Потврђено је да у испитиваном температурном опсегу наведени модели дају добре резултате.

(Примљено 5. маја 2016, ревидирано 30. јануара, прихваћено 7. марта 2017)

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