



J. Serb. Chem. Soc. 84 (3) 317–326 (2019)
JSCS–5186

Journal of
the Serbian
Chemical Society

JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

UDC 539.196–71:678.744+546.212:532.13:
536.7

Original scientific paper

Ionic-interaction of aqueous and alcoholic poly(vinyl alcohol) in the presence of protons

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(Received 1 April, revised 29 September, accepted 7 November 2018)

Abstract: The ionic-interactions of acetic acid in H₂O–PVOH and H₂O–alcohol–PVOH solvent systems were studied at different temperatures by the viscosity method. The viscosities of the poly(vinyl alcohol) (PVOH) were increased with increasing concentration of PVOH and decreased with the increasing concentration of acetic acid. The viscosity data were used to evaluate the ion–ion interactions and ion–solvent interactions in terms of the *A* and *B* coefficients of the Jones–Dole equation, respectively. The negative values of the *B*-coefficient increased with increasing temperature, showing that the acid behaves as a structure breaker in PVOH–solvent mixtures and consequently, the values of the *A*-coefficient were decreased with increasing temperature. Thermodynamic parameters, such as energy of activation (E_a^*), Gibbs energy change of activation (ΔG^*) and entropy change of activation (ΔS^*) were also calculated as a function of the acid (CH₃COOH) concentration, PVOH composition, alcohols and temperature.

Keywords: viscosity; alcohols; ion–solvent interaction; thermodynamic parameters.

INTRODUCTION

Polymeric materials are widely used in many fields due to their vast applications.^{1,2} Poly(vinyl alcohol) (PVOH) has unique characteristics of excellent filming ability, good water solubility and viscoelastic property.^{3–5} It is a highly hydrophilic, non-toxic and biocompatible polymer, which makes it industrially important and it is used in sizing agents and adhesives.^{6,7} These applications show the involvement of the polymer in the form of solution since the thermal degradation characteristics of PVOH limit its ability to be used as a conventional thermoplastic.

Viscosity is one of the simplest and reliable methods giving significant information about ion–ion, ion–solvent, and solvent–solvent interactions.⁸ The interaction between an ionic solute with non-ionic species in different solvent systems changes

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<https://doi.org/10.2298/JSC180401097N>

the physical and chemical properties of the system and the interactions between solute–solvent systems can be evaluated using the Jones–Dole equation.⁹

The viscosity of the polymer solution is influenced by the concentration of polymer in solution. At high concentrations of polymer, association of polymer chains starts, which results in inter-molecular interactions and decreased movement of the polymer.¹⁰ The extent of inter- and intra-hydrogen bonding between the polymer chain and water molecules decreases with increasing thermal energy. Strong inter- and intra-molecular chain hydrogen bonding exists between the polar hydroxyl groups in PVOH molecules. The solubility and viscosity of PVOH solution is dependent on two forces, the inter- and intra-chain hydrogen bonding and solute-solvent hydrogen bonding.^{11,12}

Various factors directly influence the polymer–solvent associations such as temperature, nature of the solvent, polymer composition, acid concentration and electrolyte concentration. In the present study, viscometric and thermodynamic studies of PVOH in different aqueous alcoholic solvents in the presence of acetic acid were undertaken. Ion–ion and ion–solvent interactions were analyzed by the Jones–Dole equation in terms of the *A* and *B* coefficients, respectively. The energy of activation (E_a^*), Gibbs energy change of activation (ΔG^*) and change in entropy of activation (ΔS^*) were also evaluated as a function of the concentration of acetic acid, the concentration of polymer and temperature. The results are explained in terms of structural and electrostatic interactions.

EXPERIMENTAL

Materials and methods

Pyrex A-grade quality equipment was used throughout the experiment. Methanol (AnalaR, 99.8 %), ethanol (Merck, 99.8 %), 2-propanol (Merck, 99.7 %), 1-butanol (Merck, 99.5 %), and acetic acid (Merck) were used. Poly(vinyl alcohol) (PVOH, Merck) with a weight average molecular mass of 72000 g mol⁻¹ and degree of hydrolysis of 98 % was used for the preparation of 0.5 % stock aqueous solutions of poly(vinyl alcohol) by dissolving 0.5 g of PVOH in 100 mL of solution at 80 °C under constant stirring using a magnetic stirrer with hot plate 78HW-1. Acetic acid solutions with concentration ranging from 0.1 mol dm⁻³ to 0.5 mol dm⁻³ were prepared in 0.1, 0.35 and 0.5 % PVOH solutions in aqueous and 5 vol. % alcoholic medium (methanol, ethanol, 2-propanol or 1-butanol).

A pH-meter model HI9813 was used to measure the pH values of the solutions. A relative density bottle having a capacity of 10.0 cm³ was used for the measurement of densities of solvent and solutions at various temperatures. The mass determination was made on a Sartorius electronic balance model BL-150S (Germany) with ± 0.001 g uncertainty. The density of solutions and solvents was calculated using the relation:

$$d = m/v \quad (1)$$

The viscosities of the solvents and solutions were measured using a constant volume Ostwald viscometer (techniconominal constant 0.1 Cs s⁻¹ capillary ASTM D445). The flow time of a solution between two marks was recorded using a stopwatch (Shanghai, China, having a least count of 0.2 s). Three observations were made to ensure the reproducibility of the measurements. A thermostated water bath (model YCW-01, Taiwan, R.O.C.) was used to

maintain a constant temperature, ranges from 305 to 323 K with the interval of 5 K. The viscosity of the solution was calculated using the following relation:

$$\eta = (d/d_0 t_0) \eta_0 \quad (2)$$

where, η and η_0 are the viscosity of the solution and solvent, respectively, t and t_0 are the time of flow of solution and solvent, respectively, d and d_0 are the density of the solution and solvent, respectively.

RESULTS AND DISCUSSION

The densities and viscosities of the aqueous and aqueous alcoholic poly-(vinyl alcohol) (PVOH) solutions having concentrations 0.1, 0.35 and 0.5 % in acetic acid (0.1 mol dm⁻³ to 0.5 mol dm⁻³) were measured in the temperature range 305 to 323 K at an interval of 5 K.

The results tabulated in Table S-I of the Supplementary material to this paper show that densities of the PVOH–solvent system increased with increasing acetic acid concentration and increasing percent PVOH concentration whereas decreased with increasing temperature from 305 to 323 K. The densities of aqueous PVOH solutions were higher as compared to water–PVOH–alcohol systems and decreased in the order: 1-butanol > methanol > 2-propanol > ethanol.

Dipolar attraction, van der Waals and hydrogen bonding make water denser as compared to alcohols. 1-Butanol and methanol are tightly packed as compared to 2-propanol and ethanol due to more attractive forces that result in an increase in density. 2-Propanol molecules, due to their branched structure, occupy more space and have fewer attractive forces and hence, there is more space between the molecules, hence density values are lower. Molecules of ethanol are packed loosely and occupy more space, which results in a decrease in the density of the solution.

The viscosity values of the solutions are tabulated in Table S-II of the Supplementary material, which show that the values increased with increasing percent of PVOH but decreased with increasing concentration of acetic acid and with increasing temperature from 305 to 323 K. It was observed that the aqueous medium has the lowest values of viscosities, which increased in the following order: methanol < ethanol < 2-propanol < 1-butanol.

With the addition of an alcohol, the interactions between PVOH and alcohols are increased that results in an increase in viscosity. Viscosities of aqueous and 5 vol. % alcoholic PVOH systems decreased with increasing concentration of acetic acid, due to increasing degradation of PVOH. A representative graph showing the effect of the concentration of acetic acid on the viscosities of 0.1 and 0.5 % PVOH in 5 vol. % ethanol at 305 K is shown in Fig. 1.

The increase in percent composition of PVOH caused an increase in the viscosities of the solution due to the association of the polymer molecules by inter- and intra-molecular forces in the polymer solution.

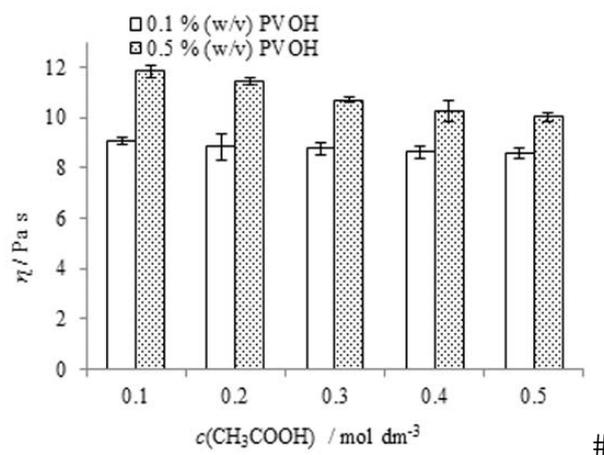


Fig. 1. A plot of viscosity vs. concentration of acetic acid in PVOH–5 vol. % ethanol solvent systems at 305 K.

Electrostatic, hydrophobic interactions, van der Waals forces and hydrogen bonding are the sources responsible for the formation of associations in polymer solutions leading to an increase in the viscosity. The results reported in Table S-II show that there is a regular decrease in the viscosities with increasing in temperature in aqueous PVOH and 5 vol. % alcoholic–PVOH solutions. As the temperature increased, due to a break down of the supramolecular structure, the intermolecular forces between solvent molecules decreased, resulting an increase in the molecular motion. Therefore, the viscosities of a liquid were found to decrease. Viscosity is affected by many factors as shown by the relation:¹³

$$\eta = \eta^0 + \eta^+ + \eta^A + \eta^E + \eta^D \quad (3)$$

where, η^0 is the viscosity for solvent, η^+ is the positive increase in viscosity caused by long-range electrostatic interaction, η^A is the increase due to alignment or orientation of polar molecules by the ionic field, η^E is the positive increase in viscosity due to the shape and size of an ion, η^D is the decrease in viscosity arising due to distortion of the solvent structure by the ions.¹³

The results tabulated in Table S-II also showed that the viscosities of aqueous PVOH solutions at a fixed concentration of acetic acid are lower as compared to aqueous PVOH–alcohol systems and increased in the following order: methanol < ethanol < 2-propanol < 1-butanol.

This is due to the change in the nature and extent of the interactions. In the case of aqueous, 5 vol. % methanol or 5 ethanol, the solvation power increased, respectively, and hence, the viscosities of the solutions increased. The viscosity was also influenced with the size of the molecule, and for this reason, the solutions containing 5 vol. % 1-butanol have higher values of viscosity as compared to those in 5 vol. % methanol. A representative graph showing the effect of dif-

ferent solvents on the viscosity of PVOH in an acidic medium at 305 and 323 K is shown in Fig. 2.

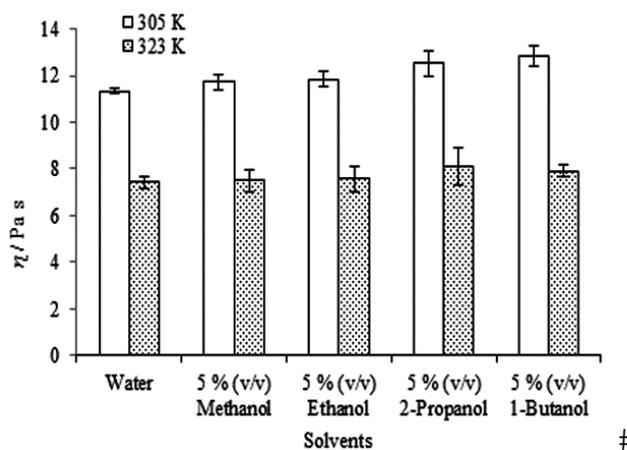


Fig. 2. A plot of viscosity vs. different solvents in 0.1 mol dm⁻³ acetic acid–0.5 % PVOH systems at different temperatures.

The increase in interaction of acid with PVOH degraded the supramolecular structure of water–PVOH system. In the case of an alcohol–PVOH system, the alcohol bound the PVOH molecules and increased the interaction between solvent and alcohol molecule, and as a result the fluidity of the solution decreased. It was observed that as the molecular weight of the alcohol increased from methanol to 1-butanol, the viscous nature of the solution increased leading to an increase in the viscosities of the solutions. The results tabulated in Table S-II showed that acid breaks the structure of resulting molecule and the viscosity of the system decreased with increasing concentration of acetic acid.

The results tabulated in Table S-III of the Supplementary material show that values of pH increased with increasing percentage composition of PVOH and decreased with increasing concentration of acetic acid. No significant change was observed on variation of the alcohol.

The interaction between water and PVOH increased with the percentage composition of PVOH, therefore, H⁺ are less available in a free condition, which results in relatively high values of pH in 0.5 % PVOH solutions as compared to the 0.1 % PVOH solutions. On increasing the concentration of acid, the number of protons in the medium increased resulting in a decrease in the pH. A representative plot showing the effect of different solvents vs. the pH of the solutions containing 0.1 and 0.5 % PVOH in the presence of 0.1 mol dm⁻³ CH₃COOH is shown in Fig. 3.

The ionic interactions of acetic acid in aqueous PVOH and aqueous alcoholic PVOH solvents were studied in terms of the *A*- and *B*-coefficients of the Jones–Dole equation expressed by the relation:^{14,15}

$$\eta_{sp}/\sqrt{c} = A + B\sqrt{c} \quad (4)$$

where η_{sp} is the specific viscosity, c is the concentration of acetic acid, and A and B are the Jones–Dole coefficients representing ion–ion and ion–solvent interactions. The linear regression method was employed to evaluate the values of the A and B coefficients from the intercepts and slopes of linear plots of η_{sp}/\sqrt{c} against the square root of acetic acid concentration. A representative plot of η_{sp}/\sqrt{c} vs. the square root concentration of acetic acid (CH_3COOH) in 0.35 % PVOH–solvent systems at 308 K is shown in Fig. 4.

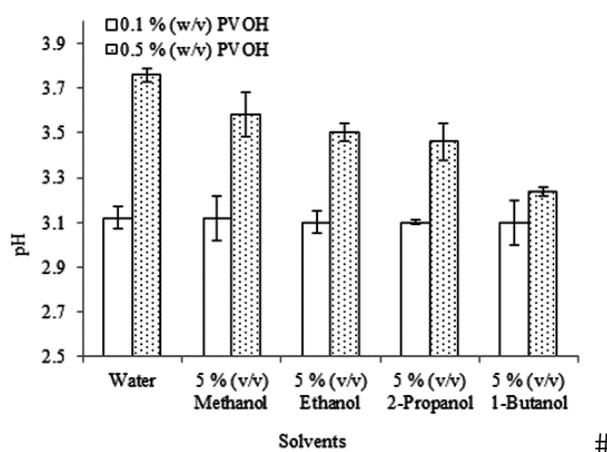


Fig. 3. A plot of pH vs. solvent solutions of PVOH in 0.1 mol dm⁻³ acetic acid.

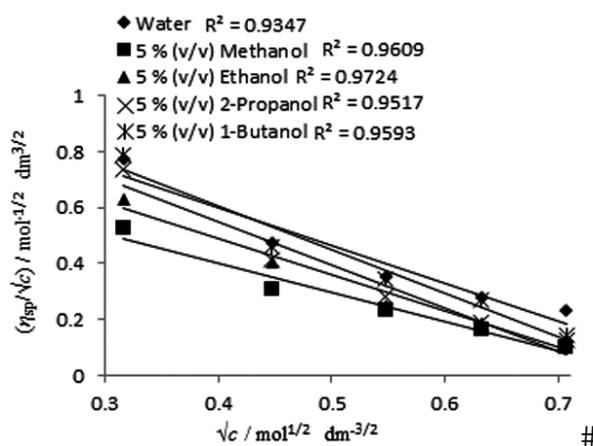


Fig. 4. A plot of η_{sp}/\sqrt{c} vs. \sqrt{c} for the 0.35 % PVOH–solvent system at 308 K.

The values of the A - and B -coefficients at different temperatures for solutions containing acetic acid and PVOH in aqueous and 5 vol. % alcoholic systems are tabulated in Tables S-IV and S-V of the Supplementary material, res-

pectively. The results show that the ion–ion interactions decreased with rising temperature and increased with the increasing concentration of PVOH. The ion–solvent interactions increased with increasing temperature and a decrease in the ion–solvent values was observed with increasing percent composition of PVOH. It was also observed that the values of the *A*- and *B*-coefficients increased as the alkyl chain of the alcohol increased. Higher values of ion–ion interactions and ion–solvent interactions were observed in water as compared to aqueous methanol and aqueous ethanol, but lower values were observed as compared to aqueous 2-propanol and aqueous 1-butanol. These results indicated that the interactions of acid are due to PVOH being less solvated in 2-propanol and 1-butanol.

The negative values of the *B*-coefficient show the association between acetic acid and aqueous PVOH and 5 vol. % alcoholic–PVOH through ion–solvent interactions. The negative the *B*-coefficient values indicate the structure breaking behavior of the acid in aqueous PVOH and 5 vol. % alcoholic–PVOH systems. The negative values of the *B*-coefficient confirmed that acetic acid in the polymer solution decreased the viscosity by degrading the supramolecular structure of the polymer in different alcohol solvents.

The thermodynamic parameters, such as energy of activation (E_a^*), Gibbs energy change of activation (ΔG^*) and entropy change of activation (ΔS^*) of PVOH solutions were evaluated by the influence of temperature on the viscosities. The values of apparent activation energy (E_a^*) of various flows were obtained by the Arrhenius relation:¹⁶

$$\eta = A \exp(E_a/RT) \quad (5)$$

$$\ln \eta = \ln(hN_A V_m) + E_a/RT \quad (6)$$

where *A* is the pre-exponential factor, *R* is gas constant, *T* is absolute temperature, *h* is Plank's constant, N_A is Avogadro's number, η is the viscosity of polymer solution and V_m is the molar volume. The energy of activation (E_a^*) and molar volume (V_m) were calculated from the slope and intercept of the plot of $\ln \eta$ vs. $1/T$. A represented plot is shown in Fig. 5.

The results for the activation energy of PVOH in aqueous and 5 vol. % alcohol containing acetic acid are tabulated in Table VI, from which it could be observed that the energy of activation of solutions containing acetic acid in aqueous and 5 vol. % alcoholic PVOH increased with increasing percent composition of PVOH. Degradation of the structure and orientation of macromolecules occur during flow and hence, positive values of the activation energy were obtained. With increasing percent composition of PVOH, the increased in activation energy may be due to the fact that at higher concentrations, a greater number of ions are present, resulting in a decrease in the ionic mobility that make it difficult to produce vacant sites in the solvent matrix that led to the higher values of energy of activation. The aqueous PVOH system had the lowest value of energy of activation, which increased with

alcohol in the order: aqueous medium < methanol < ethanol << 2-propanol < 1-butanol.

The Gibbs energy change of activation (ΔG^*) and the change in entropy of activation (ΔS^*) are expressed by the relations:¹⁷⁻¹⁹

$$\Delta G^* = RT \ln (\eta V_m / h N_A) \quad (7)$$

$$\Delta S^* = (E_a^* - \Delta G^*) / T \quad (8)$$

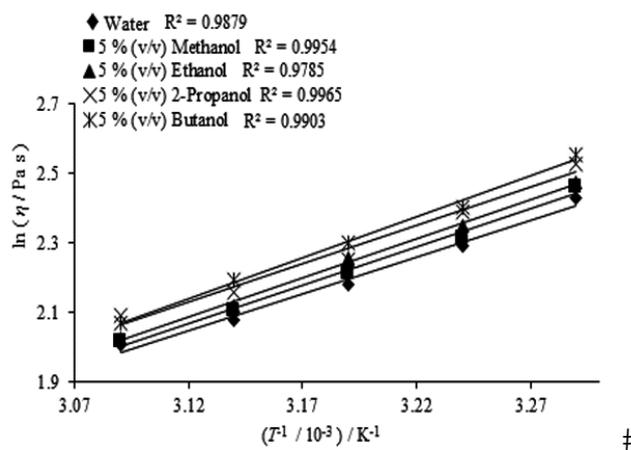


Fig. 5. A plot of $\ln \eta$ vs. $1/T$ for different mediums in 0.5 % PVOH and 0.3 mol dm^{-3} acetic acid.

The values of Gibbs energy change of activation tabulated in Table S-VI showed that an increase in the percent composition of PVOH resulted in higher values of the change in the Gibbs energy of activation. Whereas, increasing the concentration of acetic acid lowered the value of Gibbs energy change of activation. This showed that in dilute solutions, the associations were weaker and could be easily overcome during flow while in high concentration of PVOH systems, these associations were stronger and were little affected during the flow process. Therefore, the values of the Gibbs energy change of activation were high.

Negative values of the entropy change were observed in the PVOH–solvent systems. The increase in the values of the entropy change with increasing concentration of acetic acid showed the randomness of the PVOH systems and explained the structure breaking ability of acetic acid in the PVOH–solvent systems.

CONCLUSIONS

Ionic interactions of acetic acid with poly(vinyl alcohol) (PVOH) in aqueous and different alcohols were studied by viscosity method. Viscosities of solutions increased with increasing percentage composition of PVOH, and were influenced by the different alcohols in the order: methanol < ethanol < 2-propanol < 1-butanol.

Decreased viscosities were observed with increasing concentration of acetic acid and with increasing temperature from 305 to 323 K. Ionic interactions of acetic acid in the PVOH–solvent systems were evaluated in terms of the *A*- and *B*-coefficients of the Jones–Dole equation. The negative values of the *B*-coefficient increased with increasing temperature showed that the acid behaves as a structure breaker in the H₂O–PVOH and H₂O–alcohol–PVOH solvent systems. It was observed that the water–PVOH systems have lower values of the activation energy as compare to water–alcohol–PVOH systems. The negative values of the entropy change also showed the structure breaking behavior of acetic acid in the PVOH–solvent systems.

SUPPLEMENTARY MATERIAL

Additional data of the synthesized compounds are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

ИЗВОД

ЈОНСКЕ ИНТЕРАКЦИЈЕ ПОЛИ(ВИНИЛ-АЛКОХОЛА) У ВОДЕНОМ И АЛКОХОЛНИМ РАСТВОРИМА У ПРИСУСТВУ ПРОТОНА

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Јонске интеракције сирћетне киселине у H₂O– поли(винил-алкохола) (PVOH) и H₂O–алкохол–PVOH системима растварача су испитане на различитим температурама применом вискозиметрије. Вискозност раствора PVOH се повећавала са порастом концентрације полимера и смањивала са повећањем концентрације сирћетне киселине. Подаци о вискозитету раствора су коришћени за одређивање коефицијента *A* и *B* у Jones–Dole једначини, на основу којих су процењиване јон–јон интеракције и јон–растварач интеракције. Пораст негативне вредности коефицијента *B* са повећањем температуре је показао да присуство киселине нарушава надмолекулску структуру PVOH у смешама, а као последица тога и вредности коефицијента *A* су смањиване са порастом температуре. Термодинамички параметри као што је енергија активације (E_a^*), промена слободне енергије активације (ΔG^*) и промена ентропије активације (ΔS^*) такође су израчунати као функција концентрације киселине (CH₃COOH), садржаја PVOH, врсте алкохола и температуре.

(Примљено 1. априла, ревидирано 29. септембра, прихваћено 7. новембра 2018)

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